HALIDES AS ADDITION AGENTS

THE ROLE OF THE HALIDES AS ADDITION AGENTS DURING THE ELECTRODEPOSITION OF COPPER

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SCOPE AND CONTENTS:

The amount of chloride ion incorporated into a copper electrodeposit prepared from an aqueous copper sulphate solution has been determined at low chloride concentrations by the use of radiotracers. It has been found that the electrodeposits have a surface layer which is enriched in chloride ion. Evidence has been obtained that incorporation of chloride is preceded by the formation of cuprous chloride. The incorporation of chloride has been found to be increased by the presence of organic additives in the solution. The polarization during the first 30 seconds of electolysis has been interpreted using the knowledge obtained from the radiotracer work.

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I. INTRODUCTION

General Introduction

The economic importance of electrochemistry to the world today is hard to overestimate. The three industrially important processes of electrowinning, electrorefining and electroplating of metals may be mentioned. In spite of the economic importance, the procedures used are rarely based upon deductions obtained by the scientific method but upon a slowly acquired experience with the field. The use of addition agents in electrolytic solutions falls into this category. There is no knowledge available today that allows a scientist to choose the addition agent required to give the characteristics he desires. In fact the scientist is often at a disadvantage to the experienced tank house man. This lack of knowledge of addition agent action is not the result of a lack of scientific effort to solve the problem. It has been studied from before the turn of the century. Rather it reflects the difficulty and complexity of the problem. These addition agents are present in concentrations many orders of magnitude less than electrolytes, yet they completely determine the characteristics of the reactions. And what a range of characteristics may be found. They can increase or decrease the polarization; change the hardness and grain size of electrodeposited metals, the surface reflectivity, the sticking properties and many other physical properties. It is this wide range of effects that suggests the complexity of the addition agent action.

It is not necessary to state the importance of copper to the world's economy. Its useful properties of ductility, malleability, and its conductivity of heat and electricity are well known. The practical aspects of copper refining have been described by Mosher (1). The electrolytic solution is about 0.8 molar in copper sulphate and 2 M in sulphuric acid. Most refineries add salt or HCl to give a chloride content of $7 \times 10^{-4} - 1 \times 10^{-3}$ M. Glue, along with sulphonated products (thiourea, bindarene, avitone) is also added. The glue gives a fine grained deposit; the others counteract the polarizing effect of the glue. The glue added is about 0.1 lb/ton of solution and the modifying agents 2-4 times this. The current density is 16-21 ma/cm^2. The composition of the electrolytic solution has been determined by trial and error (and some luck) over the years. No one knows how the addition agents work or, what is worse, whether the composition of the electrolytic solution is the best possible. The research described in this Thesis was undertaken to learn more about the effect of the chloride addition agent during the electrodeposition of copper. It was recognized, however, that additional information might be obtained about the actual mechanism of copper electrodeposition and the mechanism of action of the organic additives since these problems could not be entirely separated. In the following sections a brief description is given of theory that is necessary to this Thesis. In the last section of this chapter an historical outline is given of work and theories on addition agent actions during the electrodeposition of copper.

Historical Background

a. The electrochemical interface

When copper metal is dipped into a copper electrolytic solution, charge separation occurs spontaneously at the interface with the result that the metal acquires a narrow band of negative charge at the surface and a diffuse layer of positive charge is formed in the solution. The establishment of this double layer takes place very rapidly (2,3). It is, of course, subject to the requirement that overall electrical neutrality be maintained. The diffuse charge in the liquid and the concentrated charge in the metal create a finite dipole moment per unit area of the interface. The two layers together form a capacitor. In order to gain an appreciation of the depth of the electrochemical interface, the separation of the two imaginary plates of the capacitor may be calculated. In Appendix I it is derived that the depth of the interface is approximately 4 Å. In a distance of this magnitude two ions could be placed side by side; but, remarkably, the interface has a considerable detail within this short distance.

The kink site: As atoms are added to a crystal lattice, they are, in the idealized case, incorporated in rows forming planes. Each row is completed before another row is started and each layer is completed before another layer starts. The point where the individual atom is incorporated into the lattice is called the kink site. It is illustrated in figure 1 (a). In order to fit into the kink site the atom must migrate along the surface of the crystal. Such an atom is called an adatom. It is illustrated in figure 1 (b). The adatom exists in a higher energy level than the atoms of the crystal. Because of this it is likely that the adatom is at least partly hydrated. It may also carry an electronic charge or part of a charge. If the adatom is charged it is called an adion. Besides having atoms at the surface similar to the underlying atoms it is possible to

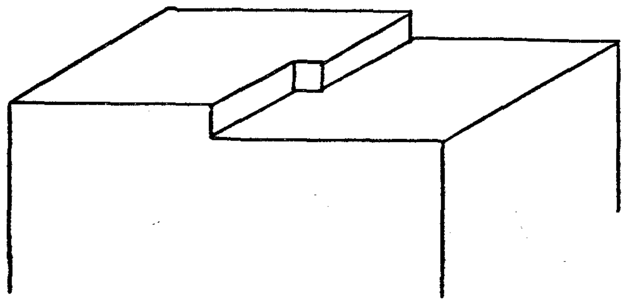

FIG. 1(a) THE KINK SITE

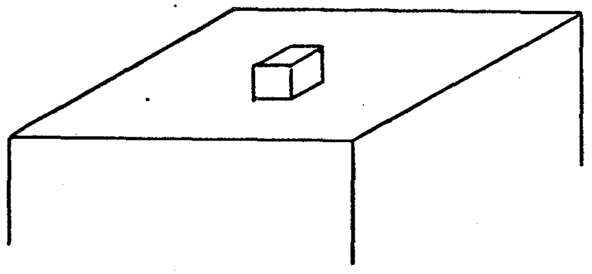

FIG 1(b) THE ADION

have foreign ions adsorbed on the surface. The question of whether these ions are physically adsorbed or chemisorbed is left to later in this chapter.

The concept of the specifically adsorbed adion is familiar (4,5,6). The sites where these adions adsorb may be described as active sites. Grahame(7), particularly, has been concerned with adsorbed anions and cations on the mercury electrode. He has estimated that the distance between the adions and the metal surface is 1-2 Å, hence it may be assumed that the possibility exists of electron sharing with the metal atoms at the surface.

The inner Helmholtz layer: The plane passing through the centers of the adsorbed anions is called the inner Helmholtz layer. Metal adatoms or adions are also located in this layer. As the charge of the inner Helmholtz layer changes, the electronic charge at the metal surface will change also, subject to the requirement of overall electrical neutrality.

The outer Helmholtz plane: The estimated free energy G of a metal cation (8), plotted as a function of the distance from the surface of the metal, is shown in figure 2. The outer Helmholtz plane is defined as the plane parallel to the metal surface through the point C. At C and to the right of C the ion is fully hydrated; to the left, the ion is removed from its outer hydration shell. The distance to C is usually several angstroms. The dielectric constant of the water in the layer to the left of C cannot be assumed to be that of the bulk because of the polarizing effect of the electric field in this region.

The energy required to bring an ion from a position in the solution to the position of specific adsorption is composed of two terms, the chemical energy and the electrostatic energy terms, and may be written as

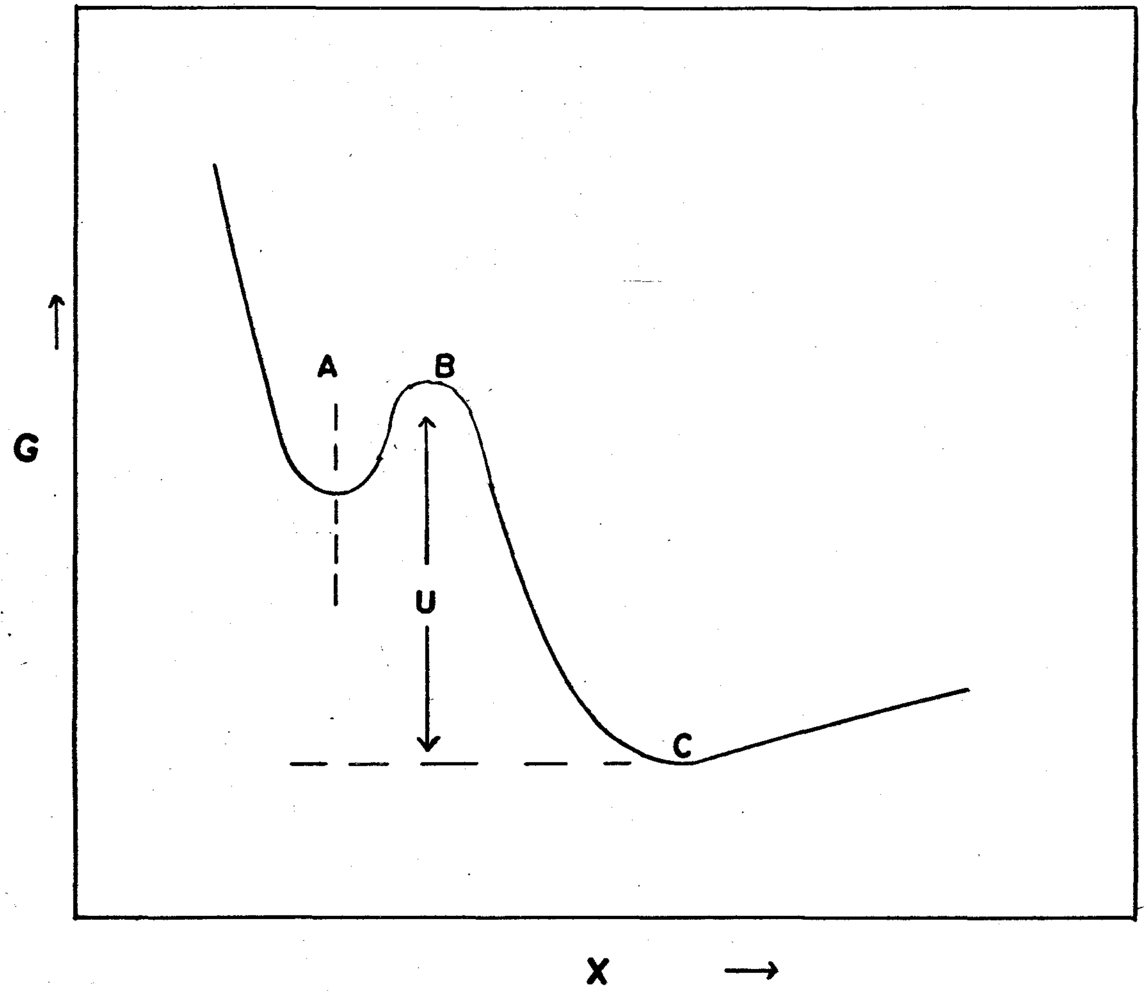

Figure 2. CHEMICAL FREE ENERGY OF AN ION NEAR A METAL SURFACE.
A. Inner Helmholtz plane C. Outer Helmholtz layer
ABC. Potential Barrier.

$H \pm Ze_o\lambda\psi$. Here H is the change in chemical energy, ψ is the potential between the electrode and the solution, λ is the fraction of this potential which acts on an ion going towards the metal, Z is the charge on the ion, and e_o is the electronic charge. The potential energy of the charged particles in the double layer is composed of the long range coulombic interactions and the short range chemical interactions of the homopolar type. The total electrostatic energy content of such a system is (9)

$$F^{el} = -1/2 \sum_{k=1}^{N} \psi_k \; e_k$$

for discrete particles and

$$F^{el} = -1/2 \int_{k=0}^{N} \psi_k \, e_k \, J_k \, dk$$

for "smeared out" charges. ψ_k here has the meaning of the electrostatic potential of all the charges except k, and J_k is a volume element.[1]

The double layer, however, is usually more complex than two layers separated by a short distance. The adions may be thought of as adding a third layer between the other two. In fact there is a grading process; the relative position of the different species is determined by the equilibrium between the short range chemical forces and the long range electrostatic forces.

A close relationship has been shown to exist between the kinetics of the electrode process and the specific adsorption of ions as well as the structure of the double layer (10).

b. Mechanisms of copper electrodeposition

Ions in aqueous solution are surrounded by three layers; the solvent envelope, the ionic atmosphere and the solvent atmosphere. The ionic

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[1] A glossary of symbols is given on pages 102 and 103 .

atmosphere has been shown by Debye and Hückel to be described by a Boltzman distribution where the probability of the occurrence of an ion in the vicinity of the central ion is determined by the charge on the central ion. The solvent envelope is composed of a group of oriented polar solvent molecules in contact with the central ion and moving with it. The solvent atmosphere is composed of more distant solvent molecules forming a cloud which becomes distorted upon motion of the central ion. The solvent atmosphere and the ionic atmosphere are attracted to the central ion by electrostatic forces. Neither the solvent atmosphere or the ionic atmosphere can penetrate inside the outer Helmholtz layer. The solvent envelope moves with the ion to the inner Helmholtz layer. It is this solvent envelope which allows adions to exist in equilibrium with the metal.

There are two models of electrolytic crystal growth. In model A the ions are transferred to the metal surface and become adions or adatoms which then diffuse to kink sites where they become incorporated into the lattice. In Model B transfer occurs direct to the growth sites. Provided that any step prior to transfer cannot be rate controlling it is apparent that in model A either transfer or diffusion may be the rate determining step; in model B transfer must be rate determining. Bockris (11,12) is the chief proponent of model A; several authors have suggested models similar to B (13,14). Hurlen (15,16,17) has proposed a "kinetic unit equation"

$$2\ \mathrm{Cu} = 2\ \mathrm{Cu}^{++} + 4e^{-}$$

that appears to require direct transfer.

The difference appears to arise from the interpretation of polarization versus current density curves. O. R. Brown and H. R. Thirsk (18), by the use of the rotating electrode, observed a decrease in current density at constant potential as the speed of rotation increased. Their interpretation is that at the higher velocities a cuprous intermediate, present at the surface of the electrode diffuses away from the surface. Although the results cannot be considered as conclusive, the evidence appears to favour model A.

The mechanism of crystal growth from the vapour phase has been studied in some detail (19,20,21,22,23,24). Crystal growth from an aqueous solution cannot be assumed to be similar, however. The solvent envelope and the double layer in which fields of the order of 10^7 volts/cm. can occur are complicating factors.

The first step in crystal growth from solution (using model A) is the adsorption of the ion onto the crystal plane. From thermodynamic arguments Bockris (25) indicates that, at least near the reversible potential, transfer will occur to the crystal plane in preference to the other four possible sites; the step site, the edge vacancy, the kink site and the surface vacancy. These adions move to step sites and diffuse along the step to a kink site. Repetition of this procedure results in incorporation of the atom. The surface transfer is energetically the more feasible because the adion (from space-filling models) is able to retain all its solvent envelope except for one of the molecules. As the adion moves to steps and then to kink sites it loses more of its solvent envelope and must at the same time lose some of its charge. At the kink site the atom may retain 3 molecules of its solvent envelope. Final incorporation in the lattice requires the atom to lose all its solvent envelope. These steps are shown in figure 3. Frank (23) has shown that the supply of step sites is practically inexhaustible for a polycrystalline surface.

It has been estimated by Bockris (26) that the direct transfer of

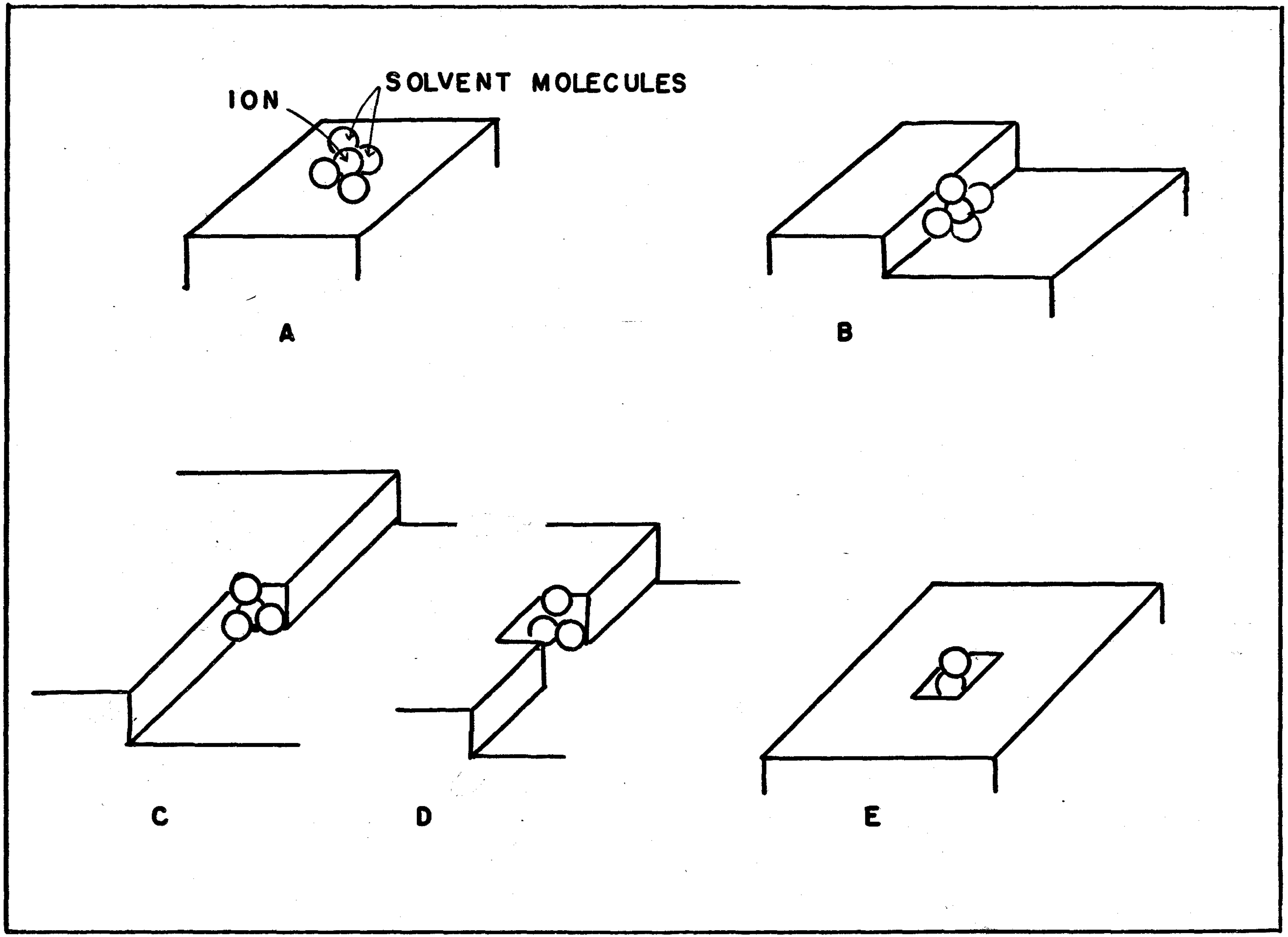

Figure 3. TRANSFER OF AN ION TO: A. Plane surface B. Step site C. Kink site D. Edge vacancy E. Surface vacancy

CAPTION TO FIGURE 4[1]

Potential energy profile diagram for Cu^{++} deposition via the redox step involving Cu^{+}. I, the initial state; the outer hydration layer displaced at D. aa', bb', cc' is the potential energy profile for Cu^{+2} deposition via Cu^{+} adions transferred to a plane surface site; xx' yy' is the profile for Cu^{+2} deposition via Cu^{+} adions transferred to an edge. a and x are the potential energy curves for the Cu^{+2} ion in its hydration shell in the initial state of the redox step $Cu^{+2} + e_m \rightarrow Cu^{+}$. a' and x' are the potential energy curves for the Cu^{+} in the final state of the redox reaction. b and y are the potential energy curves for Cu^{+} in the initial states of the transfer reaction $Cu^{+} + e_m \rightarrow (Cu^{+}_{adion} + e_m)$ at a surface or edge site respectively. b' and y' are the corresponding final state potential energy curves for Cu^{+} adions at a plane surface site and an edge respectively. cc' is the potential energy profile for surface diffusion. The fully dashed line is the free energy profile for redox and transfer steps at a surface plane.

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[1] The diagram and caption are taken from a paper by Bockris (25)

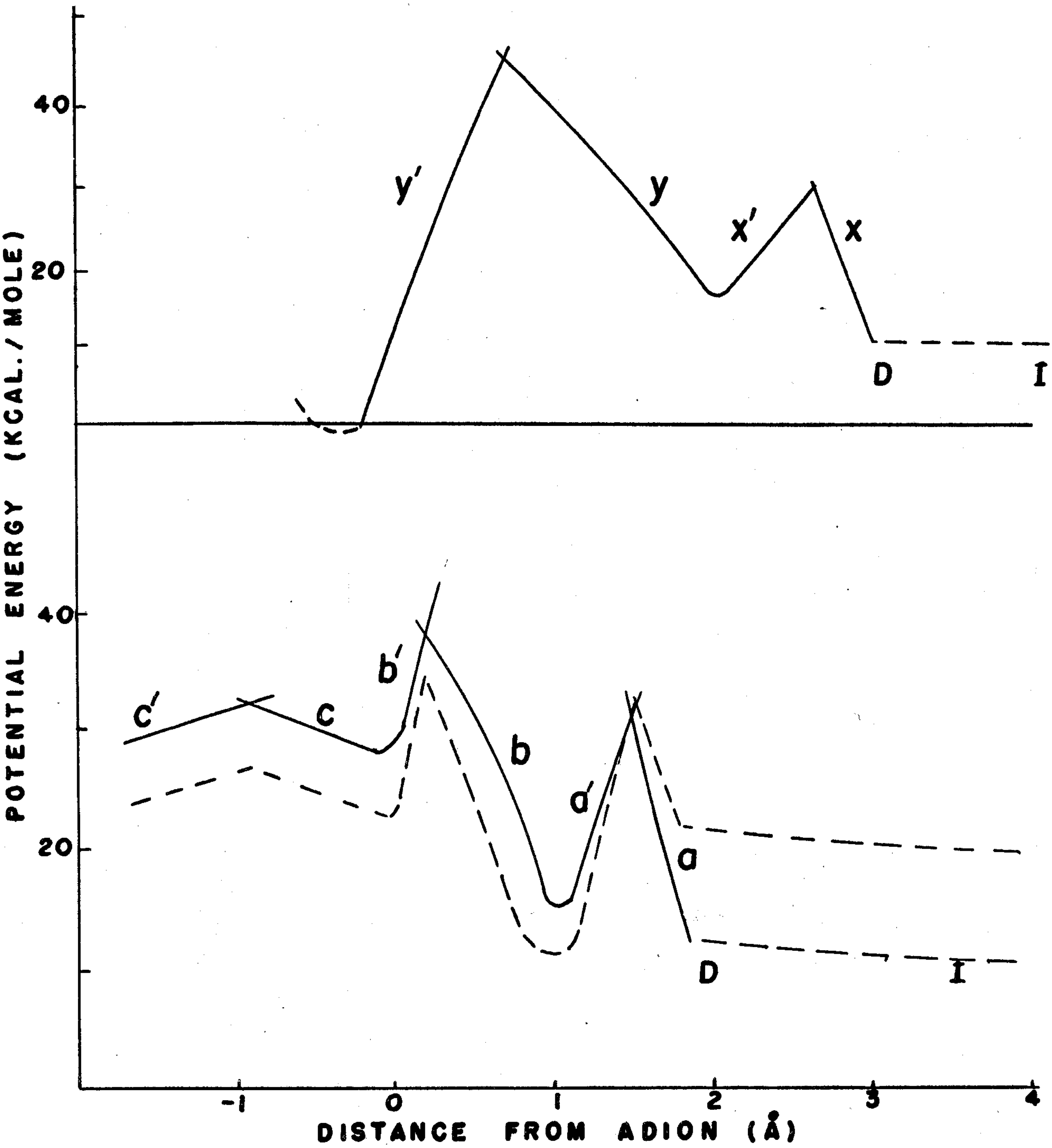

POTENTIAL ENERGY (KCAL./MOLE)
40
20
40
20
y′
y
x′
x
D
I
c′
c
b′
b
a′
a
D
I
-1
0
1
2
3
4
DISTANCE FROM ADION (Å)

Figure 4

an hydrated Cu^{++} ion to a planar adion position requires an activation energy of 100 Kcal/mole and hence is improbable. Much more probable is the formation of a cuprous intermediate, perhaps by electron tunneling with subsequent transfer of the newly formed ion to the adion position. Bockris has calculated the potential energy profile for a cupric ion approaching a copper metal surface (25). The profile is given in figure 4.

It appears that only step sites of a critical length can accept the adions (27). This is a familiar effect in the growth of crystals from the vapour phase. As the overpotential on the electrode increases, apparently the critical length decreases. This increases the number of growth sites. The number of growth sites is, of course, also dependent on the nature of the surface. Bockris also shows that the net cathodic rate of charge transfer is a minimum halfway between growth sites and that crystal growth continues after current flow has ceased (26,27).

It has been shown (28,29,30) that when copper is electroplated at low current densities onto a copper substrate the electrodeposit reproduces the crystal structure of the substrate. At higher current densities ($>$ 100 mv polarization) the electrodeposit takes on a polycrystalline structure. The first stage of the growth in the latter case is the formation of isolated nuclei within the first 15 seconds. These nuclei grow laterally until the surface is covered. After plating for one minute a layer structure has formed, and growth then appears to proceed by the edge wise movement of the layers over the surface. Impurities such as copper oxide or copper sulphide, appear to act as preferred nucleation centers.

c. Polarization, polarizers and depolarizers

Polarization is defined as the potential difference between the potential of a working electrode and the reversible potential of that electrode. The polarization of an electrode may be thought of as composed of three parts; (a) concentration polarization, (b) transfer polarization and (c) ohmic polarization, corresponding to the three steps in the discharge of an ion; (a) transport to the electrode, (b) transfer through the double layer, (c) incorporation into the crystal lattice.

Concentration Polarization: As copper ions are removed from the solution to the copper cathode, there arises a concentration gradient of copper ions extending into the solution. Since the hydrogen ion is the major charge carrier in acid solution, diffusion is the principle mechanism for copper ions to reach the double layer. The concentration gradient is controlled by the rate of discharge of the copper ions and their diffusion coefficient. The concentration polarization may be calculated. An example is included in Appendix 4.

Transfer polarization: As the cupric ion moves from the outer to the inner Helmholtz layer it is at least partly discharged. There is an activation barrier to cross. Where activation is the rate controlling step, and the cathodic current predominates, the equation connecting polarization and current density is the following: (48)

$$i = i_o \exp - \frac{\alpha Z F \eta_A}{RT}$$

which can be rearranged to give the Tafel equation

$$\eta_A = a - b \log i$$

where a and b are constants.

Ohmic polarization: The term ohmic polarization includes polarization due to surface effects and crystallization. Of the three forms of polarization ohmic polarization is the least understood. It appears that the only studies of this form of polarization has been a correlation between the total overpotential and the surface crystal structure (28,29,30). It was shown that there are four basic surface structures; ridge, platelet, blocks and polycrystalline, which are formed in turn as the polarization increases. The polycrystalline structure was observed to form at overpotentials above 100 mv. All the studies reported used copper as the base metal for copper electrodeposition. If a smooth platinum surface is used, nucleation will be required, resulting in a polycrystalline structure.

It has been indicated that transfer leads to an adion in the inner Helmholtz layer. This adion is mobile and moves across the surface to a kink site where it is finally incorporated into the lattice. It is possible (12,31) that this surface diffusion is rate determining at low current densities during the electrodeposition of copper. In the event that surface diffusion is rate determining, ohmic polarization will be the major part of the total polarization. At the more commonly used current densities, however, transfer is the principle component of the total polarization for the copper system.

The presence of certain additives in the electrolyte has been found to change the polarization and the structure of the electrodeposit. These additives either increase the polarization or decrease the polarization at the electrode. In the first case they are called polarizers and in the second, depolarizers. The polarizing additives for the copper system are generally organic material, many of them containing sulphur. The depolarizing additives usually are inorganic anions. $S_2O_3^=$ and $S^=$ are, however, polarizing agents. A remarkable fact about these additives is that their effect is very marked even at concentrations 10^{-4} - 10^{-7} times the cupric ion concentration. No satisfactory explanation is available to account for all the effects of the additives.

The actions of the additives have been variously ascribed to: (1) adsorption of the addition agent on the cathode, (2) reduction of the additive, (3) changes in the ratio of metal ions to foreign ions at the surface, (4) a bridging mechanism. A brief description of each of these is given in the following paragraphs.

In the adsorption model (32,33) it is suggested that the additives are surface active agents that preferentially adsorb on high current density peaks or growth sites. This decreases the active surface, leads to an increase in true current density and, hence, an increase in polarization. The model also accounts for the levelling and brightening action of the additives, since peaks are blocked off to growth. The adsorption of thiourea and cystine on a copper surface has been proven (34). The fact that the additives are effective at very low concentrations lends support to the idea that the additives act at the interface.

Reduction of the additive: This model is an extension of the adsorption theory. The additive is adsorbed on the copper surface and then reduced. D. R. Turner (35) ascribed the effect of thiourea and cystine to adsorption followed by reduction with the formation of CuS. It was suggested that the CuS precipitates and blocks growth sites leading to an increase in polarization. The effect of gelatin was ascribed solely to blocking of growth sites by adsorption. It has been shown (36) that sulphides are incorporated during the electrodeposition of Ni from an electrolytic solution containing thiourea.

Changes in the ratio of metal ions to foreign ions: L. B. Hunt (37) has suggested that the crystalline structure of an electrodeposit is governed by the ratio of the metal concentration in the cathode film to the concentration of the other constituents. The metal film is composed of metal ions, other cations (particularly H_3^+O), complex cations, water dipoles, and colloidal particles. Any change that results in an increase of the foreign constituents in the film causes a finer grained deposit, the result of an increased probability of nucleation. It has been suggested that all electrodeposits are crystalline (14).

The bridging role: J. Heyvrosky (38) first suggested that the depolarizing effect of chlorides and bromides results from the anion acting as a bridge for electron transfer between the cation in solution and the cathode. Such bridges, which supposedly act to reduce the activation energy of the reduction step, are well known in electron transfer reactions (39). M. A. Lashkarev and co-workers (40) use the bridge theory to explain the marked depolarizing effects of chloride in the presence of $(C_4 H_9)_4 N^+$.

d. Rüetschi's theory of electrostatic interaction in the double layer (9)

Any attempt to explain polarization phenomena requires knowledge of the energy content of a reacting particle at an electrode surface. Rüetschi uses the general interaction theory of point charge systems to calculate the electrostatic interaction energy of an ion in the double layer.

Debye and Hückel (41) determined an expression for the electrostatic potential of a central ion of charze Z_α due to its spherical atmosphere of oppositely charged ions:

$$\psi = -\left(\frac{Z_\alpha e_o}{D}\right) K$$

where e_o is the electron charge and K has the meaning of a reciprocal length defining the effective radius of the ionic atmosphere

$$K^2 = \frac{4\pi}{VDkT} \sum_i N_i Z_i^2 e_o^2 \quad .$$

V is the total volume of the system, D is the dielectric constant and N is the number of ions in the atmosphere. This expression for K is correct only for spherical symmetry. In general K is a function of the geometry of the system and will have a different expression for an ion near an electrochemical interface because of the change in geometry. The electrostatic energy content of a particle may be found by the energy required to charge the ion.

$$\mu_i^{el} = \int_0^{Z_i} \psi_s(\lambda)\, e_o Z_i \, d\lambda$$

$$= \frac{Z_i^2 e_o^2}{2D} K$$

In words, it may be said that the electrostatic energy of the particle is one half the product of the charge of the particle, and the potential from the surrounding charges.

Particles in the Double Layer: The ideal double layer may be imagined as two very thin layers of opposite charge separated by a distance d. By the foregoing it can be seen that the total electrostatic energy of the system is:

$$F^{el} = -1/2\,(\psi_+ Q_+ - \psi_- Q_-)$$

$$F^{el} = -1/2\ \psi_d Q_+$$

where ψ_+ is the potential at the positive plate, ψ_- is the potential at the negative plate, ψ_d is the potential between the plates of the capacitor and $Q_+ (=Q_-)$ is the total charge on the positive plate. The energy per charge pair is given by

$$\mu^{el} = \left(\frac{\partial F^{el}}{\partial N_+}\right)_{\psi_d} = \frac{\psi_d\, e_o Z_+}{2}$$

A real double layer is more complex than the ideal double layer described above. In fact there is a "grading process" whereby anions and cations of varying complexity form layers at a distance (see figure 5) from the electrode surface such that the coulombic attraction or repulsion is balanced by the short range chemical forces. This more complex double layer may be thought of as a series of ideal double layers and the above expressions are still valid.

Application to Treatment of Electrochemical Reaction Rates: The average electrostatic energy of one pair of the reactants in the interface can be written as

$$\mu^{el} = -\frac{Z\, e_o}{2}\ (\psi_+ - \psi_-)$$

Now $\psi_+ - \psi_-$ may be written as $(1 - \gamma)\Delta\psi_d$ since only $\Delta\psi_d$ is measurable. The term $1 - \gamma$ is the fraction of the overall voltage change due to the presence of foreign ions that affects the energy of the reacting ions. γ in practice will be a small fraction. The sign of γ will be determined by the charge of the foreign ions. For the ideal double layer, of course, γ has the value zero.

If we now introduce a short range chemical activation term, Δu^{Chem}, and apply the statistical equilibrium theory of reaction rates (42), the

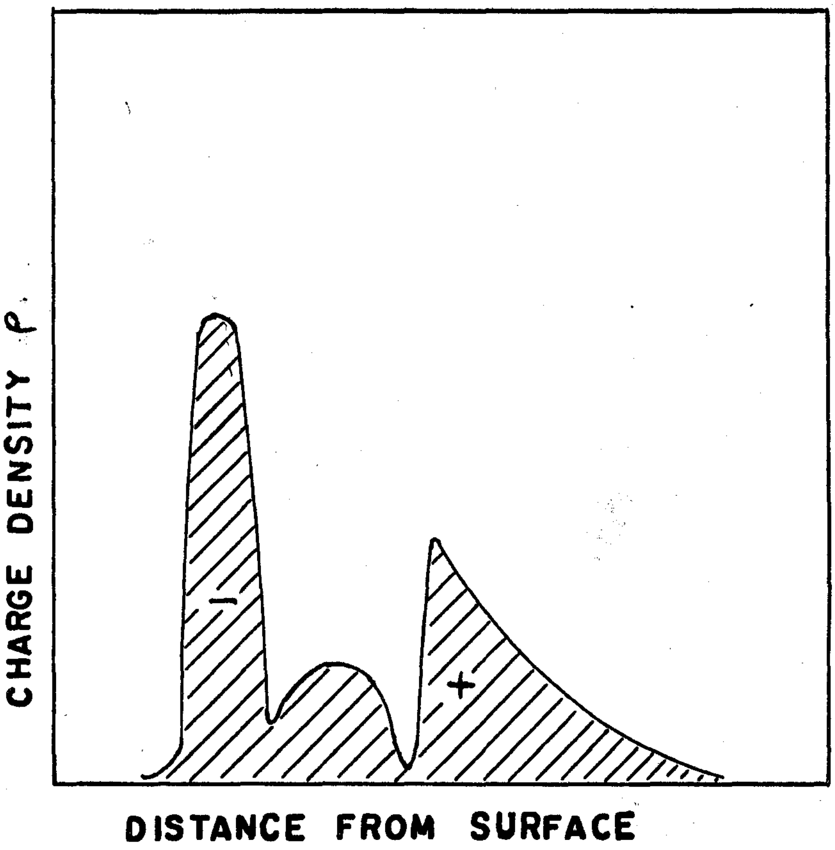


Figure 5. AN HYPOTHETICAL ELECTROCHEMICAL INTERFACE

following relationship may be written

$$i = A \exp\left\{ - \left[\Delta\mu^{\mathrm{Chem}} - Z\, e_o\, \Delta\psi_d\, \frac{1-\gamma}{2} \right] \Big/ kT \right\} \quad .$$

From comparison with the following equation (Appendix 2)

$$i = A \exp\left\{ - \left[\Delta\mu^{\mathrm{Chem}} - Z\, e_o \Delta\psi_d\, \alpha \right] \Big/ kT \right\}$$

we see that the factor $\frac{1-\gamma}{2}$ is equivalent to the transfer coefficient α. Rewriting the equation in terms of polarization η ($= Ze_o\Delta\ _d$) we get

$$\eta = \frac{2}{1-\gamma} \left(kT\, \ell n i - kT\, \ell n\, A + \Delta\mu^{\mathrm{Chem}} \right)$$

and it is seen that if γ is negative the polarization decreases, and if it is positive the polarization increases.

e. Physical adsorption, chemisorption and surface theory: When two immiscible phases are brought into contact it is nearly always found that the concentration of one component is greater at the surface than in the bulk. This tendency to accumulate at the interphase is called adsorption. In general, if the heat of adsorption is comparable to a chemical bond (greater than about 10 Kcal/mole) adsorption is classified as chemisorption. Heats of adsorption below 10 Kcal/mole are generally classified as physical adsorption resulting from Van der Waals forces (43).

Localized and nonlocalized adsorption: The surface of any solid can be considered to have variations in its potential energy as suggested in figure 6(a) for a perfect surface and in figure 6 (b) for a real surface. An adsorbate may be localized or nonlocalized on the surface. For nonlocalized adsorbates motion may consist of sliding on the surface or "jumps" through one of the phases. The same surface may give rise to localized adsorption for one adsorbate and nonlocalized adsorption for another adsorbate if their potential energy in the bulk phase differs. Adsorption

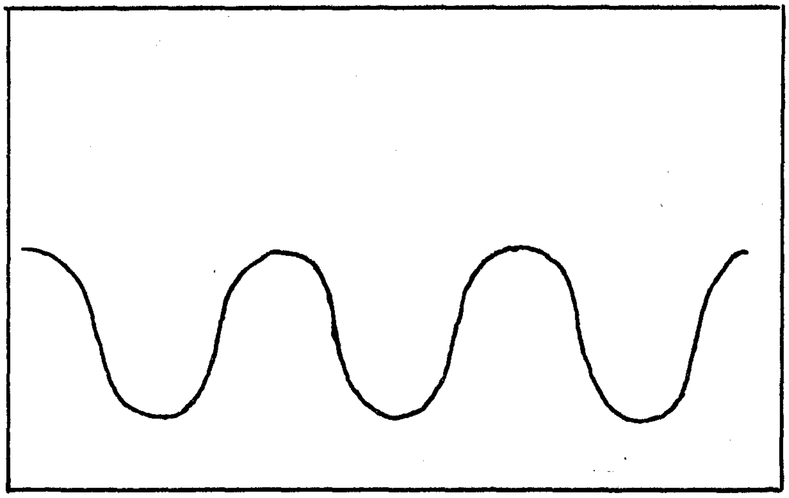


Figure 6(a). IDEAL SURFACE

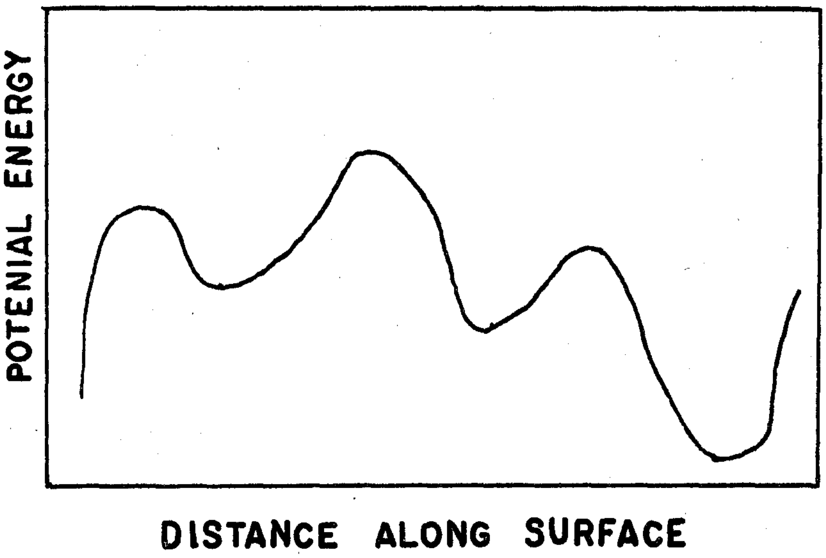


Figure 6(b). REAL SURFACE

onto a surface is not always restricted to a monolayer since subsequent layers may be adsorbed by Van der Waals forces. If this is the case, an adsorption isotherm will have the shape shown in figure 7. The horizontal part of the curve corresponds to saturation of the first layer.

f. Studies of addition agents

This section will give a chronological outline of investigations of the action of certain addition agents during the electrodeposition of copper onto a copper cathode.

The first detailed study of chloride as an addition agent was reported by Yao in 1945 (44,45). Until that time it had been widely believed that chlorides precipitated antimony in the electrolytic solution as antimony oxychloride and thus prevented antimony from codepositing with the copper. Yao showed that the chlorides did not do this. He also found that the halides, excluding fluorides, increased the cathode polarization, and that there was a correlation between grain size, hardness and polarization. A break in the polarization curves was found at approximately 9 mg. Br^-/l., 15 mg. Cl^-/l. and 22 mg. I^-/l. which represented the maximum polarizing action of the halides. Yao explained the variation in the polarization on the assumption that the equilibrium between cupric and cuprous ions is slow and that in its place the following reaction occurs,

$$Cu^{++} + 2X^- + e^- = CuX_2^- \qquad \text{Where } X^- = Cl^-, Br^-, I^-.$$

The polarization data that Yao published, however, has not been observed by others (46). It is possible that traces of Ag^+ in the solution lead to these results. If Yao had observed the strong polarization action of the organic additives, and the equally strong depolarizing action of the halides in the presence of the organic additives, it might have occurred

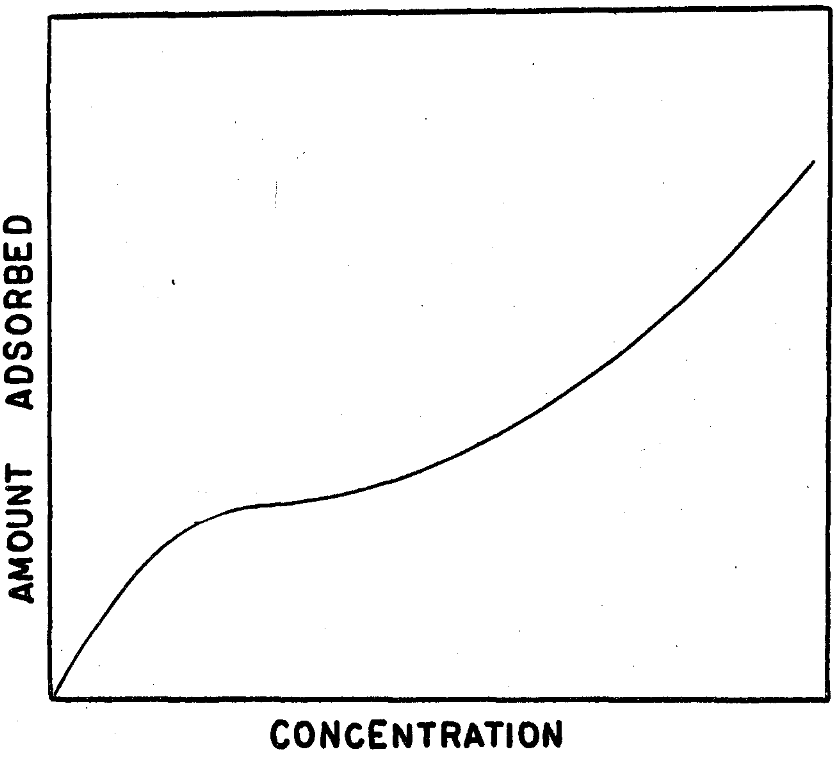


Figure 7. AN ADSORPTION ISOTHERM WITH MULTILAYER ADSORPTION

to him that the halides lowered the polarization to a value where reduction of antimony could no longer occur.

In 1947 Heyvrosky (38) published a paper in which he showed that the presence of halides tended to make the polarographic reduction of metal salts essentially reversible. He concluded that the halides were acting as electron bridges and thus facilitated the reduction of the metal cations.

In 1954 Shreir and Smith (47) published the results of a study of the cathode polarization and superficial structure of the electrodeposit resulting from the presence of addition agents. They concluded that addition agents fall into one of four groups; (1) those with no apparent effect (glucose, acetonitrile), (2) those which increase the polarization η and lead to finely crystalline electrodeposits (amino and and hydroxy acids), (3) those which increase η and lead to microcrystaline deposits (high concentrations of sodium thiosulphate or thiourea) and (4) those which increase η and lead to coarsely crystaline deposits (low concentrations of sodium thiosulphate, thiourea, hydrogen sulphide or carbon disulphide). In explaining these effects it was suggested that the addition agents adsorb on the surface at first inhibiting crystal development. For class (4) it was suggested that the agent was adsorbed and became complexed with incoming cations forming an ion more difficult to reduce. Upon reduction the addition agent transferred to another cation and the process repeated.

In 1952 Gauvin and Winkler (46) published data on the cathode polarization versus chloride concentration. They showed that the chloride is a depolarizing agent. The maximum depolarizing action was found at a chloride concentration of 20mg/l. They suggested that the following equilibrium was set up at the cathode

$$Cu^{++} + Cu \rightleftarrows 2\ Cu^{+}$$

It was estimated that the cathode layer concentration of Cu^{+} is 0.65×10^{-3} gm.mole/l. From the solubility product of CuCl it was estimated that precipitation of CuCl should occur when the Cl^{-} concentration exceeds 2.5×10^{-4} gm.mole/l.(8.8mg/l.) assuming that the chloride concentration was the same in the cathode layer as in the bulk of the solution.

Mandelcorn and others (48) in 1952 published the results of an investigation of the polarization as a function of halide concentration in the presence of gelatin. They attributed the increase in polarization observed in the presence of gelatin alone as the result of an increased current density because part of the active area of the cathode was covered with adsorbed gelatin. They interpreted the decrease in polarization on addition of halides as resulting from an increase in the active area of the cathode by the activation of more inert positions. It was suggested that this was brought about by production of lattice imperfections and the increase in polarization observed with further addition of halides was the result of formation of adsorbed cuprous halides.

In 1955 Sukava and Winkler (49) published the results of an investigation of the polarization in the presence of cystine and chloride. Of interest is a graph of the steady state polarization (after 3 hours) versus the chloride concentration which is shown in figure 8. The minimum in the curve occurred at a chloride concentration of 12mg/l (3.4×10^{-4} moles/l.). The interpretation given for the increased polarization caused

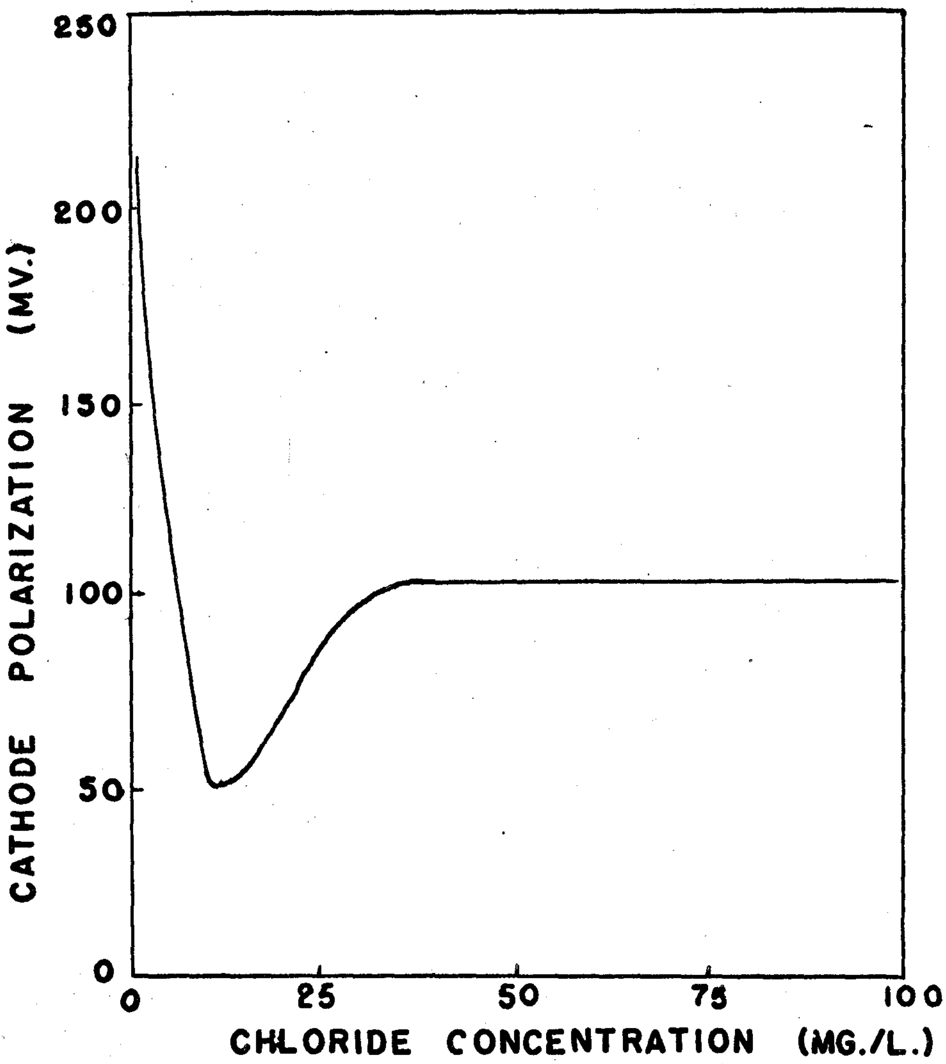


Figure 8. STEADY STATE POLARIZATION IN THE PRESENCE OF CYSTINE AND CHLORIDE (Sukava and Winkler, 49)

by cystine was that a cystine-copper complex formed that was less readily discharged than the aquo complex. The addition of chloride was postulated to give rise to more easily discharged chlorocomplexes which resulted in lower activation and lower concentration polarization.

In 1959 Ke and others (34) published the results of an investigation of the role of thiourea in the electrodeposition of copper. They showed that thiourea is adsorbed on the copper surface and shows no preference for any crystal face. It was also shown that the presence of thiourea destroyed the natural tendency of copper to continue the base structure and resulted in a microcystalline structure showing a uniform bright polycrystalline surface. It was suggested that the adsorbed thiourea interferes with the crystal growth of the copper electrodeposit.

Turner and Johnson (35) in 1962 published the results of an investigation of the effects of addition agents on the kinetics of copper electrodeposition from sulphates. Some of their data is shown in figure 9. It can be seen that thiourea and cystine give rise to a Tafel slope and exchange current considerably greater than for the additive free solution. They suggested that the additives containing sulphur are reduced at the cathode forming CuS which precipitates on the surface and interferes with crystal growth.

Shanfield and Lighty (50) have shown that the presence of trace impurities leads to an increase in the number of growth hillocks on the surface of a copper electrodeposit. An investigation of the depolarizing effect of chlorides during the polarographic reduction of metals (51) has lead to the suggestion of the electron bridge model. In 1965 Gorbunova and Sutiagina (36) published results showing that thiourea was decomposed

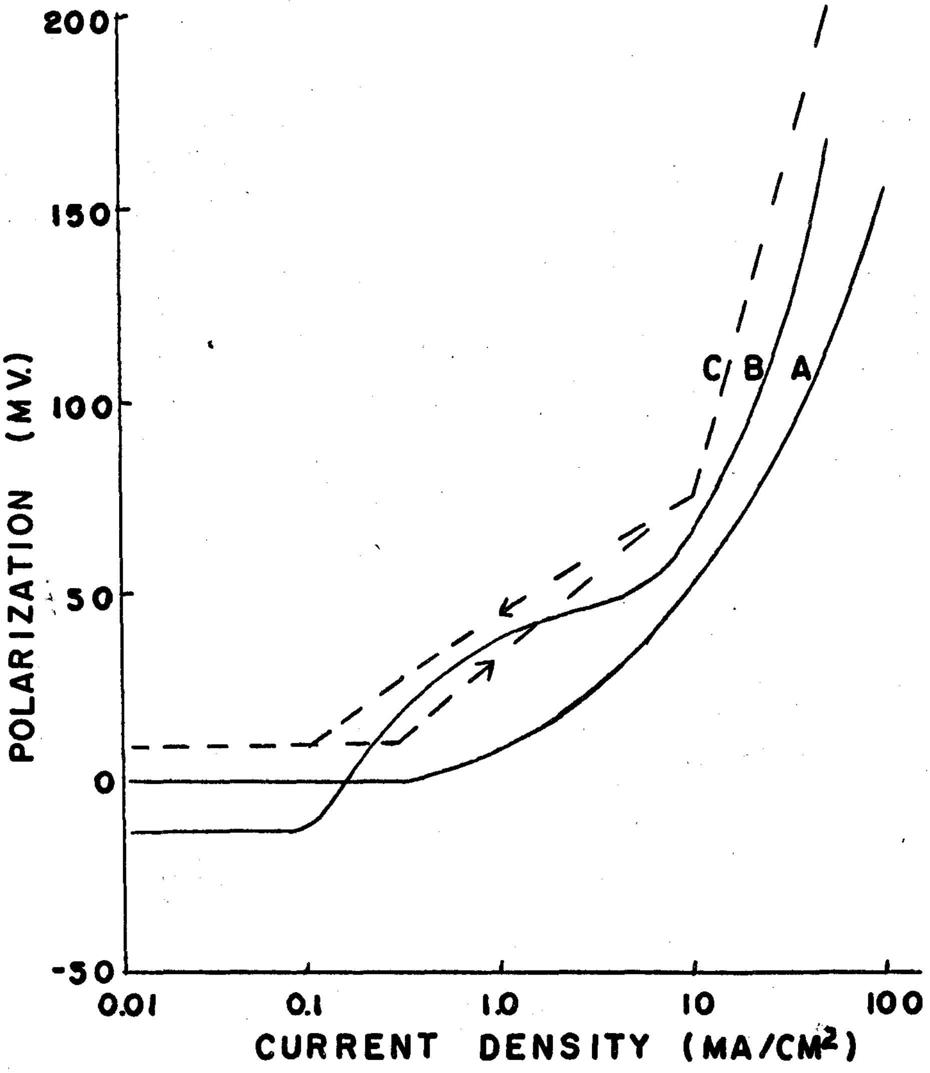


Figure 9. TAFEL PLOTS OF THE POLARIZATION IN THE PRESENCE OF ADDITIVES.
A. No additive B. 4×10^{-4}M thiourea C. 4×10^{-4} cystine

at the cathode during the electrodeposition of Ni. They measured the total amount of sulphur and the amount of sulphide in the electrodeposit and showed that nearly all the sulphur was present as sulphide.

To summarize, it may be seen that mechanisms have been proposed for addition agent action. Predominating are the views that; (1) the additives are surface active and reduce the active area of the cathode, (2) the additives are reduced at the surface and the reduction products, incorporated in the electrodeposit, interfere with crystal growth, (3) complex ions either of greater difficulty to discharge or with lower diffusion coefficients are formed, (4) the halides increase the active area, (5) the halides act as electron bridges. Common to all the theories, however, is that the additives act at the interface between the metal and the solution.

II: EXPERIMENTAL

Electrolytic Cell and Circuit

Preliminary investigations were carried out using a Haring cell (52) and a Sanborn series 150 galvonostatic recorder. It was decided, however, that the cell was unsuitable for several reasons. (1) The cell was made of plexiglass and was very difficult to clean after use with surface active addition agents. It was found that the cell had to be washed with 1:1 HNO_3 and then placed in running water for 24 hours in order to give reproducible results. (2) The construction of the cell was such that there was a strong convection current at the cathode and an air-solution interface on the electrode. It seemed inevitable that oxygen diffusing into the electrolytic solution at the meniscus and the wetting of a small part of the electrode above its surface would lead to spurious results. (3) The reference electrode was situated some distance from the cathode so that the IR drop was an appreciable fraction of the potential measured. It also was unsatisfactory to have the reference electrode immersed in the bulk solution since the presence of addition agents would change its rest potential. (4) The cathode surface was difficult to reproduce with this type of cell.

A new cell was designed to overcome the problems found with the Haring cell. (1) It was made of pyrex glass so that it would be easy to clean. (2) A Luggin capillary was used so that the reference electrode could be placed in a separate solution. (3) The electrodes were made of platinum so that the copper electrodeposits could be stripped from it with

1:1 HNO_3. (4) The cathode was arranged so that it could be removed and placed in position for end window Geiger counting.

A line diagram of the cell is shown in figure 10. It can be seen that the cell was made in three compartments connected by glass joints. It was not entirely satisfactory to have these glass joints because it was necessary to use some lubricant on them. The very minimum amount of lubricant (yellow lubriseal) was used and this was placed only on the outer edge of the joints. It was felt that the solution which entered the joint by capillary action would not mix with the bulk. The reproducibility of results indicated that no contamination was introduced from this source.

A description of the electrode compartments follows. The cathode and anode compartments were similar. The electrodes were platinum discs, 2 cm. in diameter cut from 0.01" platinum metal that had a smooth polished surface. A platinum wire of 0.01" radius was carefully spot welded to the center of the disc. These electrodes were then centered in the electrode compartment. All the compartments were made from 4 cm. diameter pyrex tubing. The cathode compartment met several other requirements dictated by the measurements to be made. The electrode was mounted so that the distance between the surface and the end of the Luggin capillary was 5 mm. The surface of the cathode also extended 1 cm. beyond the end of its glass compartment so that when radioactive material on the electrode was counted there would be no appreciable scatter from the glass. The end of the compartment was flat so that it could be placed on end for counting the cathode. Since electrical connections were made through the end of the electrode compartments, a connection through mercury was used. To count activity on the electrode, the cathode compartment was removed from the cell (after

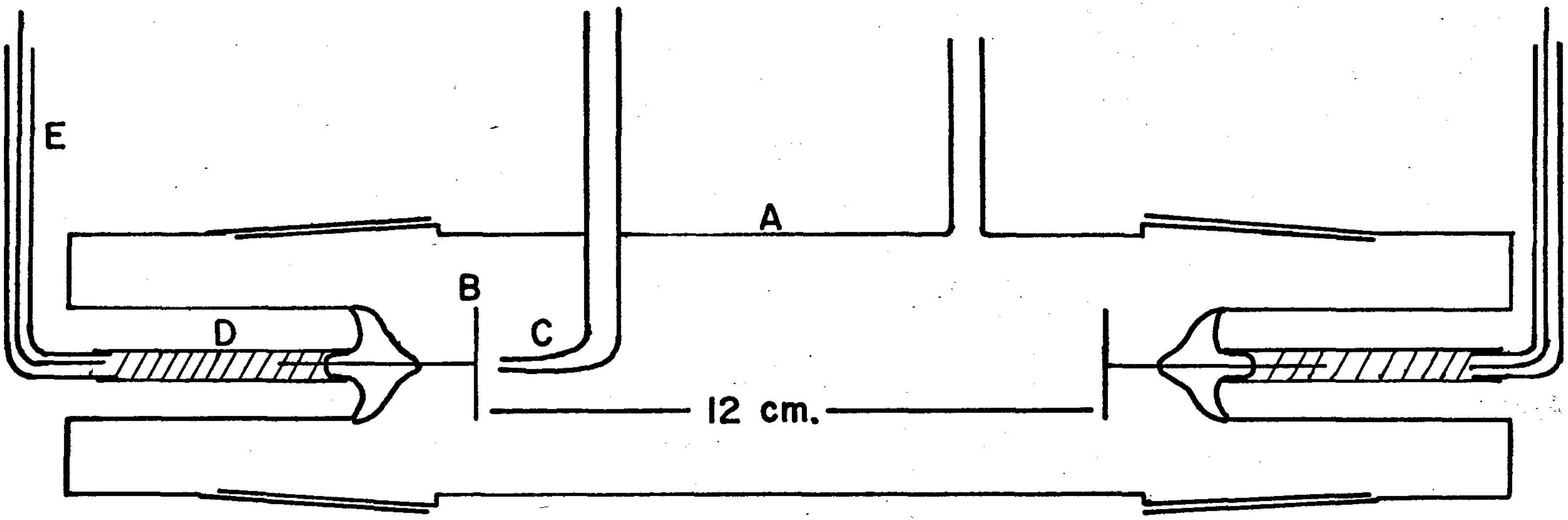


Figure 10. THE ELECTROLYSIS CELL A. Pyrex glass tubing B. Platinum Electrode C. Luggin capillary D. Tubing containing mercury E. Glass envelope containing connecting wire

emptying out most of the solution), and the glass enclosed connecting wire and mercury removed. The compartment could then be placed on end.

The Luggin capillary of the middle compartment was carefully centered. The other end of the tube curved over to the side and dipped into a beaker containing the reference electrode and electrolytic solution. A short open ended glass tube was added to the center compartment for adding or removing solution and also to allow for a tube through which gas could be bubbled into the cell. Short pieces of clamped rubber tubing were placed over the end of the tubes when necessary to close them off, but the rubber at no time came into contact with solution in the cell. Stop cocks were not used as they might have been a possible source of contamination.

The current was supplied by a 12 volt lead storage bettery, kept - when not in use - close to a full charge by a trickle charger. Current control was maintained by a set of two watt carbon resistors and a 60 ohm 12 watt rheostat for fine control. It was found necessary to have the large rating for the rheostat in order to minimize temperature dependent changes in resistance after current began to flow. Current was measured with two milliameters, one a Triplet in the range 0-100 ma. and one a Simpson in the range 0-200 ma. Both meters were carefully calibrated using a Leads and Northrop decade resistor precise to ± 0.1% and a Minneapolis-Honeywell model no. 2746 potentiometer. Only the mid-range of the meters was used. With this arrangement, current could be known and controlled within ± 3%.

The reference electrode was a piece of copper wire mounted in a glass envelope so that only 1/2 in. was exposed to the electrolytic solution.

The wire was electroplated from the standard solution before use. The polarization between the cathode and the reference electrode was measured using a Tektronix type 502 dual beam high gain oscilloscope with an input resistance of 1 megohm. Photographs of the oscilloscope trace were taken with a polaroid model 196A camera. Low capacitance shielded cable was used to make connections between the oscilloscope and the electrodes.

Solutions

The standard solution contained 125 gm. $CuSO_4 \cdot 5H_2O$ and 50 ml. conc. H_2SO_4 per liter. It was therefore 0.5M in Cu^{++} and 0.93M in H_2SO_4. Fischer certified reagent grade $CuSO_4 \cdot 5H_2O$ and CIL reagent H_2SO_4 were used to make up the solution. The specified maximum chloride content of these was 0.0005% and 0.2 ppm respectively. Doubly distilled water was used to make up the solutions. A few of the earlier results were obtained with a solution made with water distilled from alkali, but for the remainder the water was distilled from an alkaline permanganate solution. The standard solution was discarded if not used within ten days.

Liter quantities of CIL reagent HCl and Fischer certified HBr were made up. The solutions were standardized from time to time using the Volhard method (53). Purified gelatine, Fischer certified reagent l - cystine or certified reagent thiourea was added to the electrolytic solution in the required amount shortly before use.

Production of Radioactive Material

Radioactive chlorine and bromine were used in the experiments. Samples were obtained by placing 4 ml or less of either the HCl or HBr solutions in a polythene capsule. This capsule was then placed in a larger polythene capsule called a rabbit. Irradiations were carried out using the rabbit system of the McMaster Swimming Pool Type Reactor which had a flux of about 10^{13} neutrons/cm^2-sec at the rabbit position used. The length of irradiation varied from a few seconds up to 8 minutes depending on the quantity and type of material irradiated. Samples less than 100 μc were obtained and, because of the short half-lives involved, were used shortly after production. Decay schemes of the isotopes used (Cl^{38}, Br^{80}, Br^{80m}) are given in Appendix number 3.

Counting Procedures

Counting of the activity in the cathode was done using a Tracer Lab type TGC1 end window Geiger tube mounted in a 1-3/4" thick lead shield and connected to an Electronic Associates type SC3T scaler. The TGC1 is a self-quenching Geiger-Mueller tube having an effective window diameter of 1.1" and a window thickness of 2.5 mg/cm^2. The recommended operating voltage was 1500 volts and the minimum plateau length 300 volts.

The sample counting efficiency may be related as follows (54)

$$Q = (y)\ (E)\ (O)\ (G)\ (S)\ (U)$$

where the symbols have the following meaning:

Q counting efficiency,

y detectable radiation yield per disintegration,

E counter efficiency for the radiation,

O fraction of radiation lost from counter dead time,

G geometry factor,

S scattering factor,

U the fraction of radiation not absorbed before reaching the counter.

For most of the experimental work a reference sample of the same active material as found in the cathode was used. Under these conditions y and E may be assumed to be the same. Calibration for dead time losses was done by the paired source technique. The dead time $\mathcal{T}$ is obtained from the equation

$$\mathcal{T} = \frac{n_1 + n_2 - n_T - n_b}{n_T^2 - n_1^2 - n_2^2}$$

where n_T is the rate for both sources together,

n_b is the background rate,

n_1 is rate for source 1 plus background,

n_2 is rate for source 2 plus background.

From a knowledge of $\mathcal{T}$ a graph of corrected count rate versus observed count rate was constructed. This graph was used for correction of both chlorine and bromine count rates.

To correct for the geometry factor and the scattering factor, a 100λ sample of active chlorine solution adsorbed on a piece of filter paper was counted on a planchet in the standard reference position. Then 100λ of the same solution was placed on another piece of filter paper fitted to the surface of the cathode, and its count rate determined. The count rate of the electrodeposit and the solution used in its plating were counted in these same positions. The amount of halide in the electrodeposit was determined from the following relationships:

$$\frac{\text{count rate of } 100\lambda \text{ solution on the electrode}}{\text{count rate of } 100\lambda \text{ ssolution in the reference position}} = N$$

$$\text{Amount of halide in the deposit} = \frac{R_1}{R_2} \times \frac{A}{N}$$

where R_1 is the count rate of the electrodeposit on the cathode,

R_2 is the count rate of the 100λ of the plating solution,

A is the amount of the halide in 100λ of the plating solution.

The above procedure will be accurate if the absorption and scatter of the β radiation from the filter paper placed on the cathode were the same as that from the electrodeposit on the cathode. The error introduced by this procedure is small for bromine and chlorine activities since the energies of the radiations are large (smallest is the 1.11 MeV. β from chlorine) and the scatter in both cases is primarily from the platinum cathode. Both the filter paper and the electrodeposit were thin. Any error introduced from this source would be such that the estimated halide in the electrodeposit would be slightly low for all measurements by a constant amount. It was also assumed that the difference due to absorption in the approximately 1 cm. of air difference between the reference and the cathode positions was negligible for the hard β radiation.

The method of obtaining solution samples for counting is described in the last section of this chapter.

Experimental Procedure

a. Polarization measurements

Approximately 320 ml. of the standard electrolytic solution were placed in a polythene squeeze bottle. The amount used was obtained from the weight of the bottle before and after the solution was added and from the density of the solution (1.12 gm/cc.). If an addition agent was used the required amount was weighed out and added. The anode was plated (usually at approximately 30 ma/cm^2) from standard solution contained in a beaker using a platinum wire as anode. Sufficient copper was plated onto the anode to last for a given experiment. To prevent any edge effects the cathode, before plating, was entirely covered with a layer of paraffin wax except for a circle of 2.55 ± 0.15 cm^2. area on its face. The cathode was electroplated in a manner similar to the anode but the current density of

8 ma/cm^2 and the time of 5 minutes were carefully controlled. In this manner it was felt a uniform reproducible surface was prepared. The surface always appeared bright and polycrystalline. The cathode was then added to the cell and the cell was filled with electrolytic solution leaving a narrow air space at the top. The reference electrode was placed in a 100 ml. beaker containing approximately 60 ml. of standard solution. The cell and reference solution were then placed in a water bath. The Luggin capillary tube was filled by forcing solution from the cell into it. Electrical connections were made and a small tube was inserted into the cell so that helium could be bubbled through the solution. The primary purpose of the helium was to provide a steady rate of stirring. After approximately one half hour wait the shutter of the camera on the oscilloscope was opened, the current was turned on to the preset current density for 50 seconds and then switched off. The shutter of the camera was closed 10 seconds later. (A sweep rate of 2 sec./cm. was used). A carefully measured amount of HCl or HBr solution was then added and after another half hour wait the next polarization measurement was taken. The half hour wait between measurements was probably longer than necessary, but it was essential that the solution (stirred by helium bubbling) become uniform throughout the bulk between measurements. The water bath was a large 15 gallon aquarium in which the temperature could be controlled within ± 0.2 C°. The temperature was measured with a thermometer calibrated to 0.1C°. For measurements at 0°C a crushed ice-water bath was used. The concentration of halide in the cell was known from the weight of solution in the cell and the amount of halide added.

b. Incorporation measurements

The anode and cathode were prepared in a manner similar to that described above. The necessary amount of electrolytic solution, with or without additive, was placed in the polythene bottle. The required amount of radioactive halide was pipetted into the bottle and the solution was added to the cell. The cell was placed in the constant temperature bath and helium bubbling was started. A suitable delay was allowed so that the temperature of the solution in the cell reached equilibrium with the bath temperature.

After each plating, the cell was disassembled and the cathode washed in a spray of distilled water for approximately 30 seconds. The rest of the cathode compartment was carefully washed to remove any active solution. The cathode was then touched with adsorbent tissue to dry the surface. The cathode was placed in position under the end window Geiger counter inside the lead shield and the count rate determined. A reference sample (usually 100λ) of the solution was transferred to the center of a 1" diameter piece of filter paper placed in a counting planchet. The lambda pipettes used were calibrated "to contain" so they were filled with distilled water to the calibration mark and this rinse water was carefully added around the perimeter of the filter paper such that no air bubbles became trapped. In this manner a uniform and flat sample was obtained for counting. The planchet was placed in a heavy brass holder to be counted.

It was established that the amount of halide incorporated into the electrodeposit was a negligibly small fraction of the halide in most solutions. As a result it was possible to re-use these solutions. More active halide was added to the solution which had been retained in the polythene bottle. The cathode was stripped of its copper deposit with 1:1 HNO_3 and prepared as before. The cell was reassembled and the procedure repeated.

c. Adsorption measurements

Two types of surface were used in the adsorption studies. The copper surface on the cathode was prepared as described above, or a microcrystalline bright copper surface was prepared by electroplating the copper from the standard solution containing a specified amount of cystine addition agent. A beaker containing 200 ml. of the standard solution with additives was placed in the water bath. Helium was allowed to bubble slowly through the solution. The copper surface was touched dry with adsorbent tissue and quickly mounted horizontally in the solution for five minutes. The cathode was removed, washed and the halide determined as described above.

III: EXPERIMENTAL RESULTS

Preliminary Experiments

The first experiments were designed to check the radiation purity of the chloride solution and adequacy of the counting procedures. The cathode electrodeposit and a sample from the HCl solution were counted for a time sufficiently long to determine the half life. The data from one experiment are presented in figure 11. It may be seen that both samples gave good half lives over a period of 100 minutes showing that there was no appreciable amount of active impurity present. It also may be seen that no significant loss of chloride occurred from the liquid sample even though considerable evaporation took place. The half lives determined from the slopes were 39.0 minutes for the solution sample and 37.5 minutes for the electrodeposit. The accepted half life for Cl^{38} is 38 minutes.

Further experiments were designed to determine how much bromide would be removed by successive washings. In one experiment a fresh copper surface was immersed in standard solution containing active bromide. After the first washing the amount of bromide on the surface was 6.8×10^{-10} moles/cm^2 and after the second, third and fourth washing, the amounts were respectively 6.0×10^{-10}, 5.6×10^{-10} and 5.1×10^{-10} moles/cm^2. In general it was found that about 25% of the adsorbed activity could be removed from the copper surface by extended washing. When an electrodeposit was prepared from a solution containing 4.4×10^{-4} moles/l, rewashing had almost no effect.

A series of experiments was performed to determine if the active halides could be exchanged with inactive halides. The results are present-

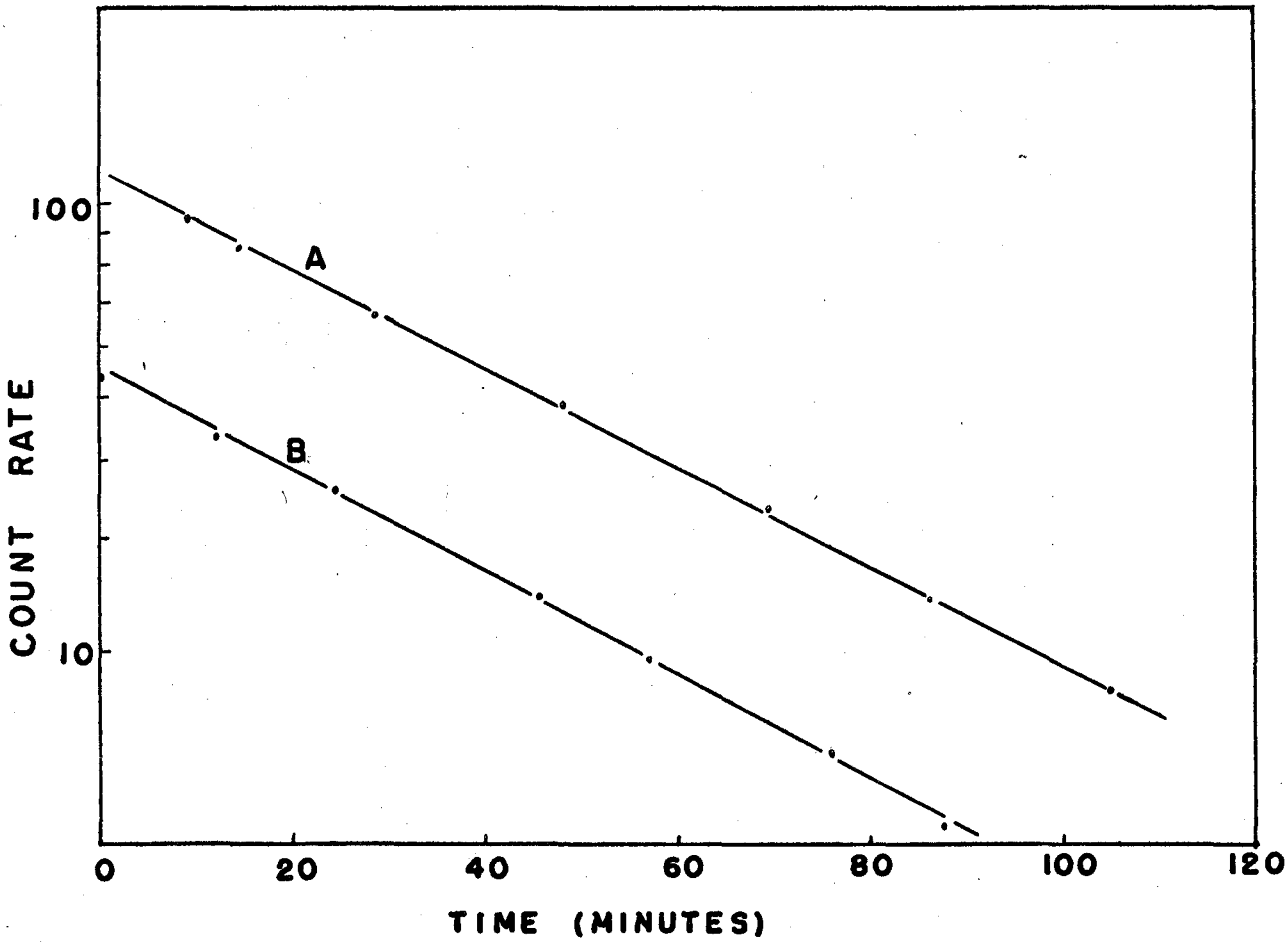


Figure 11 HALF LIFE DETERMINATIONS. A. Solution Counts B. Electrodeposit counts

ed in Table I. It may be seen that about 80% of the active halide was found to exchange from the surface during a five minute immersion in approximately o.01M KCl solution. On the other hand, only 5 - 8% of the halide was found to exchange from an electrodeposit prepared from the copper solution containing active halide. It may be concluded that most of the halide atoms in the electrodeposit were buried or strongly held at the surface.

It is well known that halides adsorb on almost any surface. Paraffin was chosen to cover the back and connecting wire of the cathode because it was expected that halides would not adsorb on the paraffin. This was experimentally observed by immersing a piece of paraffin in the standard copper solution containing active Cl^{38}. The paraffin was removed, washed, and the count rate determined. There was no detectable activity on the paraffin.

Incorporation during Electrodeposition

a. Incorporation as a function of halide concentration in the electrolyte.

The amount of halide incorporated in the electrodeposit is given in figures 12 and 13. The results are plotted as moles incorporated per cm^2. versus halide concentration in the electrolytic solution. From the amount of halide incorporated, it may be seen that there were about 3×10^4 copper atoms for each bromide and about twice this number for each chloride in the electrodeposit.

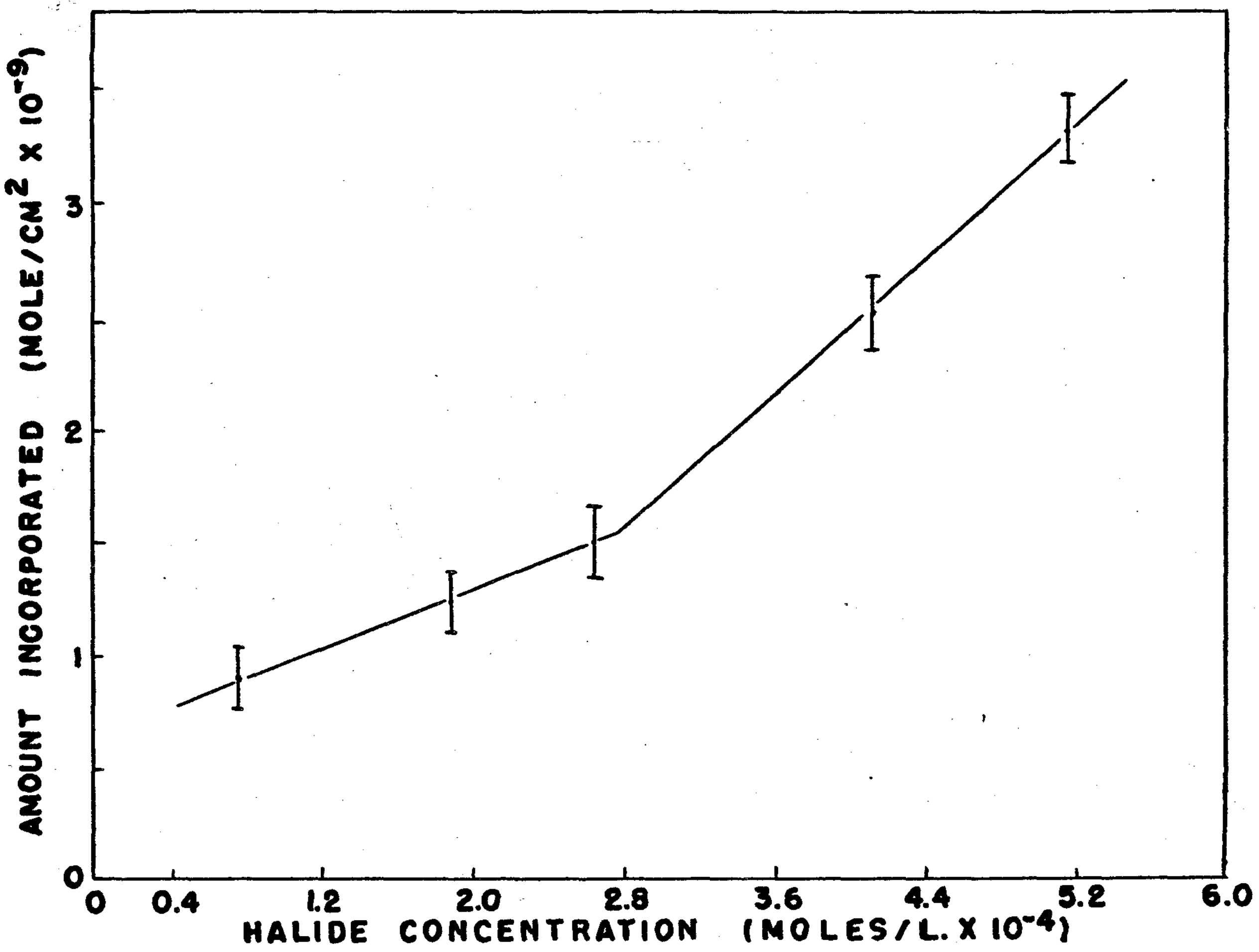
b. Incorporation in the presence of organic additives.

The amount of chloride incorporated into the electrodeposit as a function of chloride concentration in the electrolytic solution containing either gelatin or cystine is shown in figure 14. There are two features

TABLE 1: EXCHANGE EXPERIMENTS

Experiment	Surface	Solution	Quantity of Chloride (mole/cm^2)
1. Adsorption	Standard copper	Standard	4.20×10^{-10}
above immersed in 0.02 M KCl for 6.5 min.			1.17×10^{-10}
2. Adsorption	Standard copper	Standard	4.00×10^{-10}
above immersed in 0.01 M KCl for 5 min.			1.03×10^{-10}
3. Adsorption	Cystine-prepared	Standard	1.01×10^{-8}
above immersed in 0.01 M KCl for 5 min.			0.236×10^{-8}
Repeat immersion for 5 min.			0.197×10^{-8}
Repeat immersion for 5 min.			0.179×10^{-8}
4. Electrodeposition		Standard	2.73×10^{-9}
above immersed in 0.01 M KCl for 5 min.			2.63×10^{-9}
Repeat immersion for 5 min.			2.61×10^{-9}
5. Electrodeposition		Standard plus cystine	1.81×10^{-8}
above immersed in 0.01M KCl for 5 min.			1.74×10^{-8}
Repeat immersion for 5 min.			1.67×10^{-8}

Figure 12. INCORPORATION OF CHLORIDE. Electrolysis at 20 ma/cm^2 for 30 min.



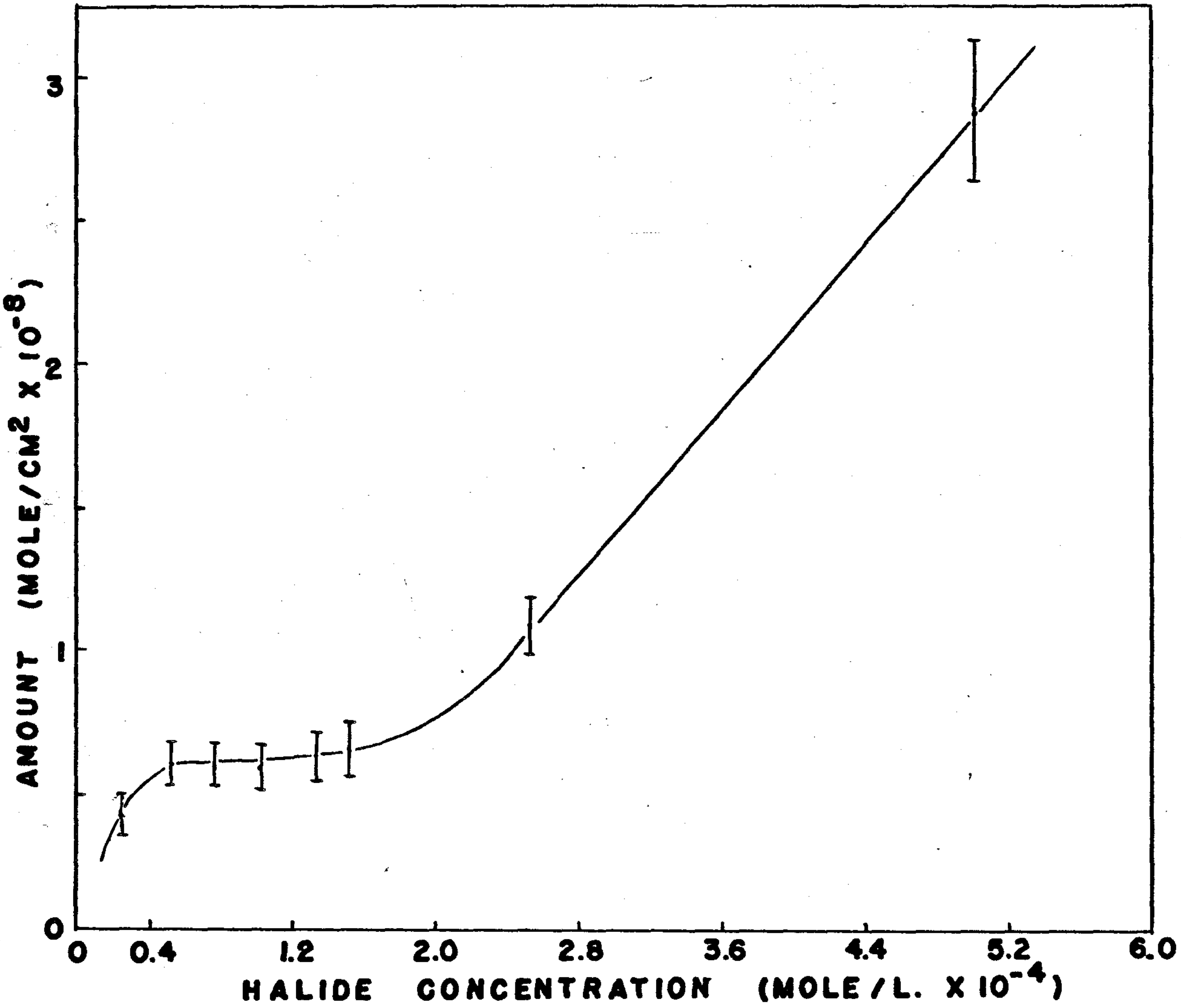
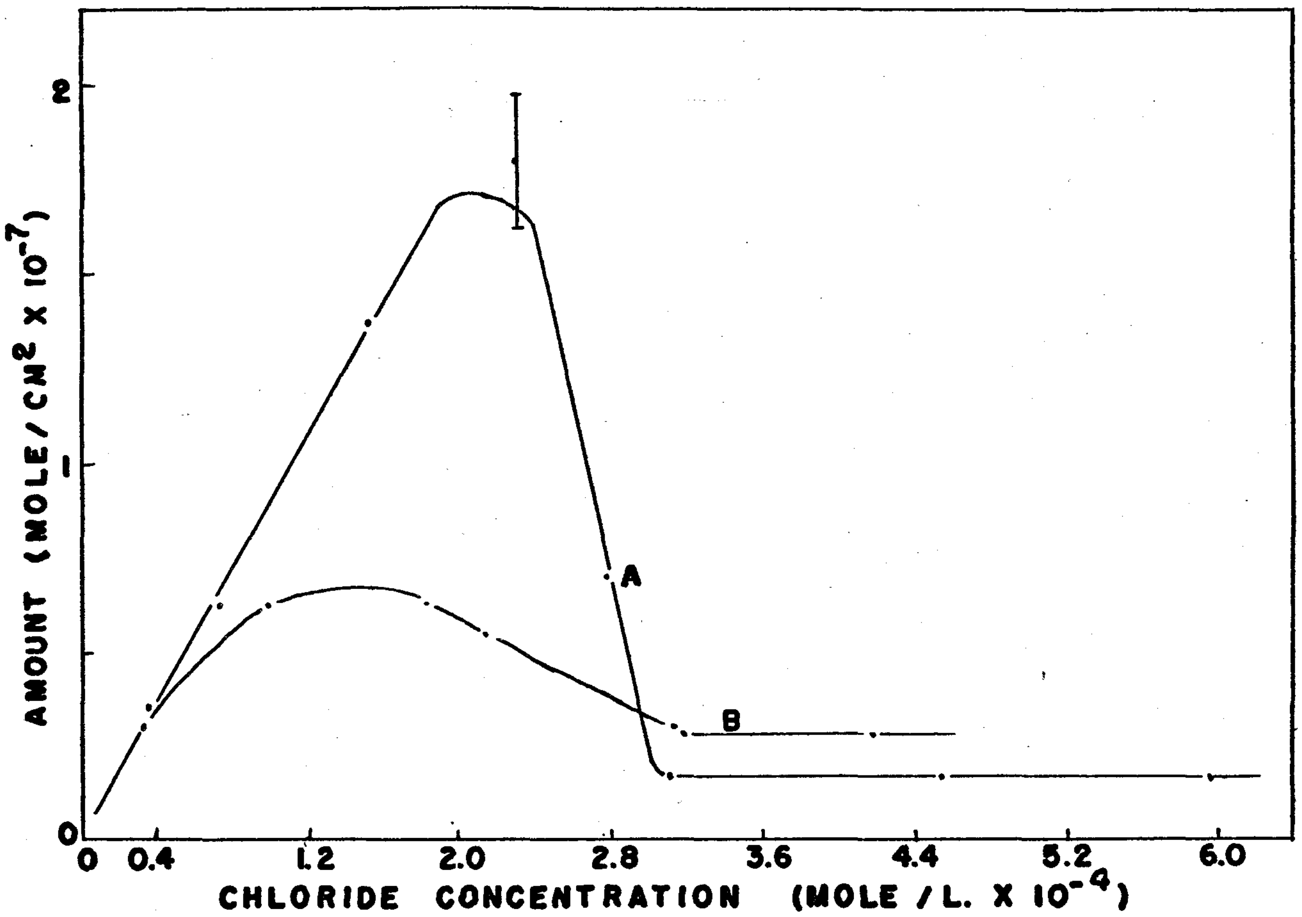


Figure 13. INCORPORATION OF BROMIDE. Electrolysis at 20 ma/cm^2 for 30 min.

Figure 14. INCORPORATION OF CHLORIDE. Organic additive present A. Cystine 95 mg/l. B. Gelatin 72 mg/l. Electrolysis 12 min. at 20 ma/cm^2



about this graph that stand out. One is the remarkable hump in the halide range 0.4 - 2.8 x 10^{-4} moles/liter. The other feature is that the amount of chloride incorporated was considerably greater in the presence of these organic additives. Because the length of electrolysis here is 12 minutes, the amount of chloride incorporated should be compared with the values given in figure 17 for the same length of electrolysis. The explanation of these features is not immediately evident and will be left to the discussion section of this Thesis.

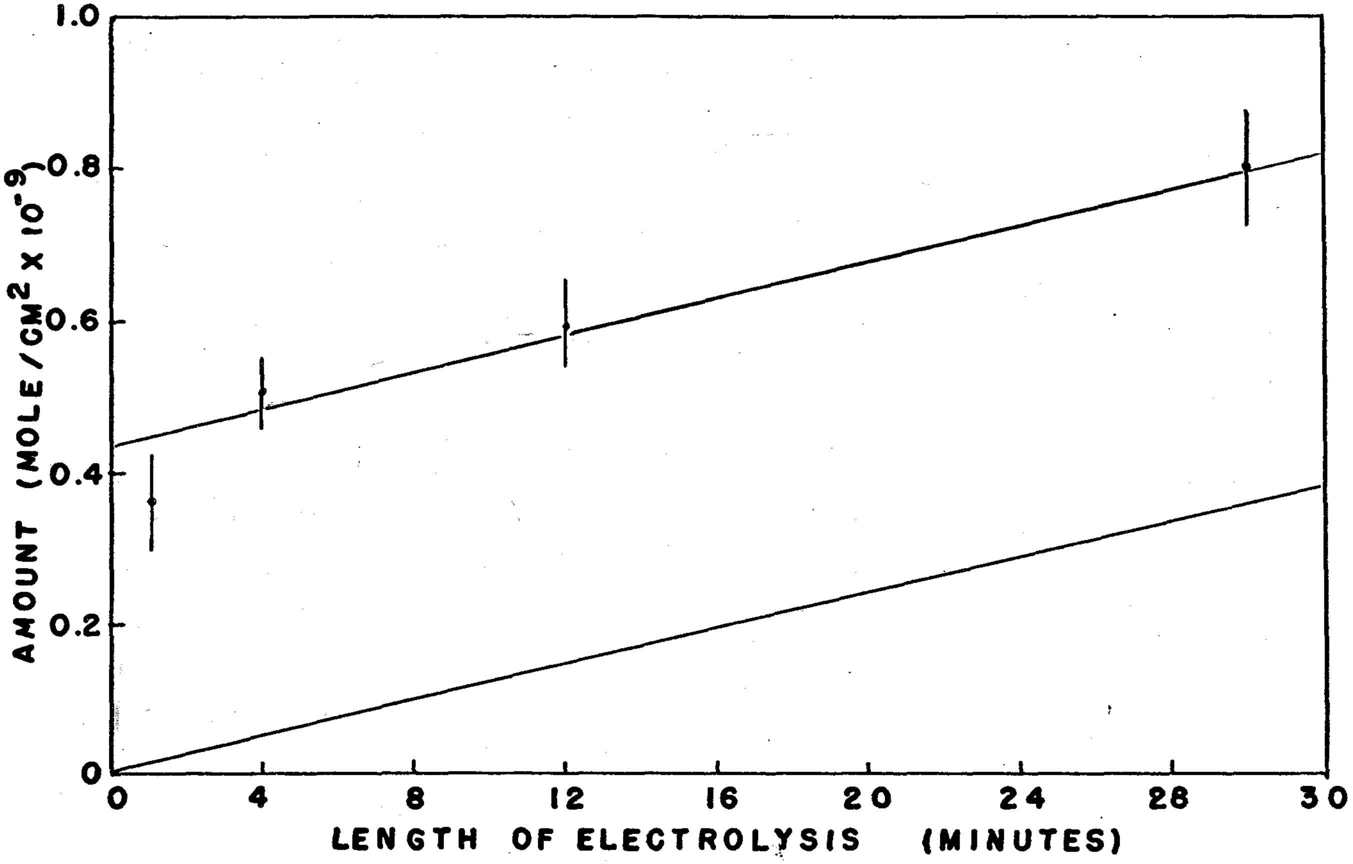
c. Incorporation as a function of the length of electrolysis.

The amount of chloride incorporated in the electrodeposit after electrolysis of varying lengths of time is given in figure 15. It is immediately seen that the amount of halide "incorporated" for zero time of electrolysis was not zero, but that the rate of incorporation was otherwise uniform. This was true of the several experiments of this type performed. This implies that either a layer of halide was buried in the first few seconds of electrolysis by a deposit of constant but lower composition, or a layer of halide remained at the surface, as the electrodeposit of constant composition grew. In order to distinguish between these two possibilities the following experiment was performed.

d. Incorporation as a function of the depth of the electrodeposit.

An electrodeposit was prepared from the standard copper solution containing 3.36 x 10^{-4} moles/liter cystine and 27.7 x 10^{-5} moles/liter HCl. To check for the existence of an adsorbed layer, the deposit was immersed in 0.01 M KCl for two five minute periods. About 8% of the activity exchanged off. To check that the copper exchange current did not affect the results the deposit was immersed in the standard copper solution for five minutes. About 4% of the activity was lost. The experiment then consisted

Figure 15. AMOUNT INCORPORATED AS A FUNCTION OF LENGTH OF ELECTROLYSIS. 20 ma/cm^2, 3.7 x 10^{-4}M Chloride



of anodically stripping the electrodeposit in steps. The results are given in figure 16. It may be seen that after 1% of the deposit had been stripped, the halide in the remaining deposit was uniformly distributed. It is conclusive that the halide was uniformly distributed in the deposit, but that there was also a tightly bound surface layer.

e. Incorporation as a function of current density.

The amount of chloride incorporated in the electrodeposit at three different current densities as a function of chloride concentration in the electrolyte is given in figure 17. (It is recognized that the amount measured includes both a surface layer and a deposit of constant composition; however, in this chapter, the word incorporated will be retained to describe the total measured amount of halide.) The length of electrolysis was adjusted so that the total amount of electrodeposited copper was the same for the three curves. The interesting feature of the graph is that the amount of chloride incorporated increased as the current density decreased for halide concentrations below about 3.6×10^{-4} moles HCl/liter. This information appeared to suggest that the halides were not being randomly trapped in the deposit, but instead were undergoing some step that, at the lower current densities, had more time to occur.

f. Incorporation from a mixture of halides.

A series of experiments was run in which a mixture of HCl and HBr was placed in the electrolytic solution and the relative amounts of the halides in the electrodeposit determined. The composition of the solutions varied slightly, but were approximately 1.3×10^{-4} molar in HCl and 5.8×10^{-5} molar in HBr. For these experiments the HBr solutions were allowed to cool for about three hours following irradiation so that the

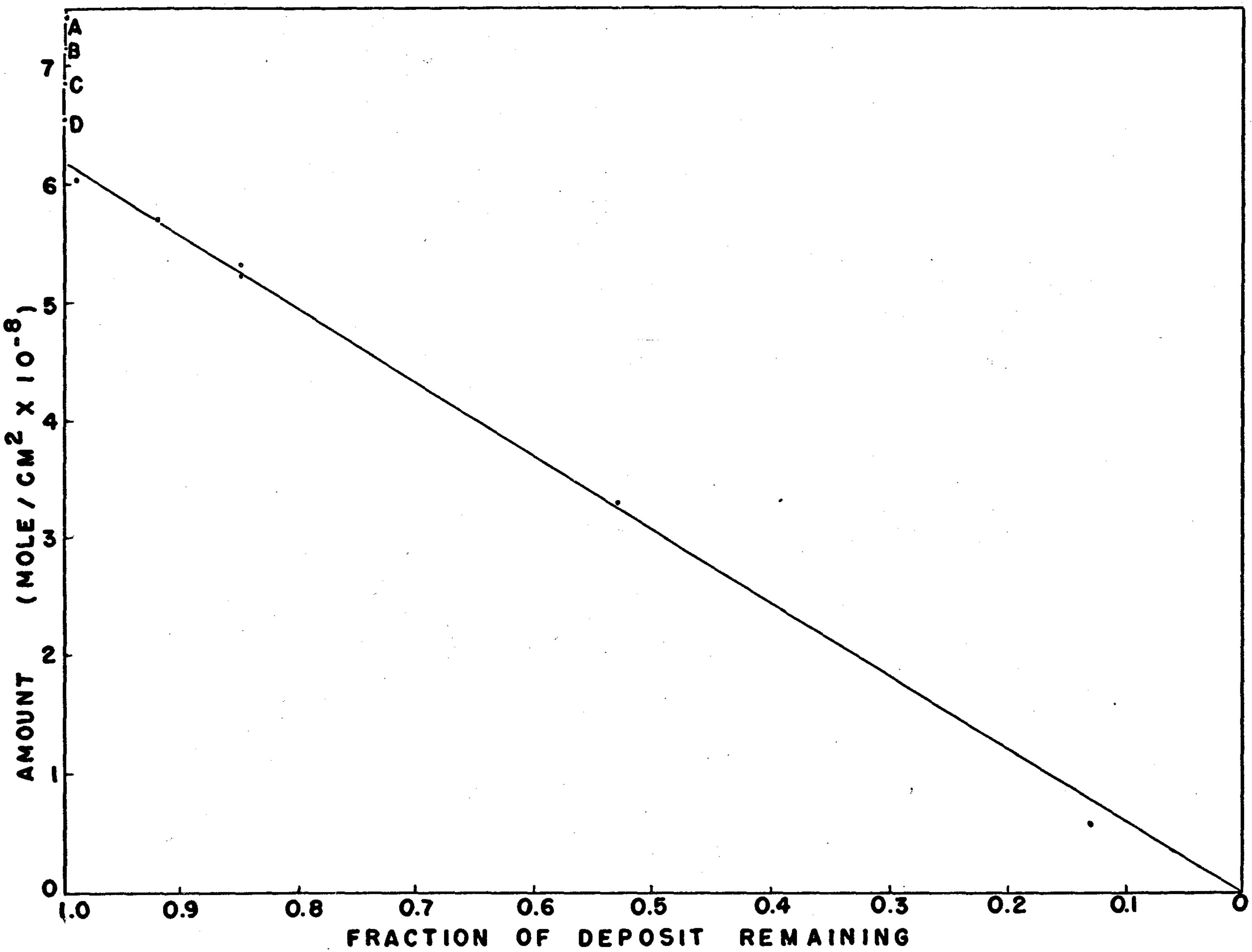


Figure 16. INCORPORATION AS A FUNCTION OF DEPTH IN THE ELECTRODEPOSIT. A. electrode washed B. after 5 minute exchange C. after 10 minute exchange D. after immersion in Cu^{++}solution.

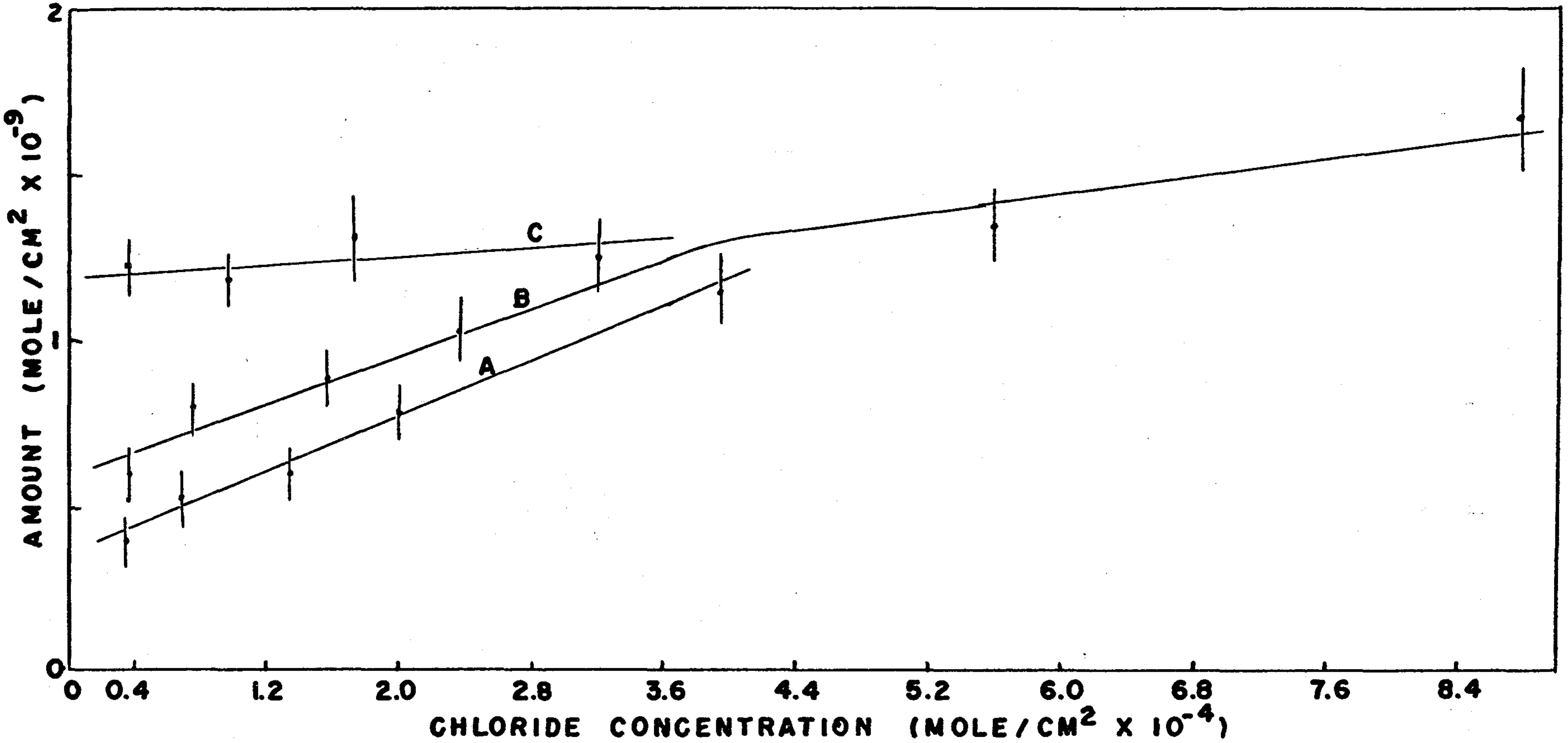


Figure 17. CHLORIDE INCORPORATION AT DIFFERENT CURRENT DENSITIES. A. 6 min. at 40 ma/cm^2. B 12 min. at 20 ma/cm^2 C. 60 min. at 4 ma/cm^2

principle activity of the samples was the 4.5 hour Br^{80m}. The relative amount of the halides in the electrodeposit was determined by plotting the count rate for a period of about seven hours and stripping the decay curves into the 4.5 hr. Br^{80m} and 38m Cl^{38}. Two examples of this are shown in figures 18 and 19. It was immediately evident from the decay curves that an appreciable bromine enrichment was found in the halide in the electrodeposit. From an examination of Table II, it may be seen that the bromine enrichment increased for the following changes; decrease in current density, and decrease in the amount of organic additive in the electrolyte.

g. Incorporation at 0°C.

The amount of chloride incorporated at 0°C and 25°C is shown in figure 20. It may be seen that the amount incorporated was greater at the lower temperature. A plot of the logarithm of the amount incorporated versus the logarithm of the chloride concentration was tried but could not be interpreted.

<u>Adsorption Studies</u>

a. Adsorption on a standard copper surface as a function of halide concentration in the electrolytic solution.

The amount of chloride adsorbed on the standard copper surface is shown in figure 21 and the amount of bromide in figure 22. The features of interest here are (1) the discontinuity in the curves at 2.8×10^{-4} moles/liter for HCl and about 1.2×10^{-4} moles/liter for HBr, (2) the amount of bromine adsorbed was greater than for HCl - varying from about three times as much at low concentrations to 30 times as much at higher concentrations.

b. Adsorption on a surface prepared with cystine.

A copper surface was prepared in the usual manner except that the

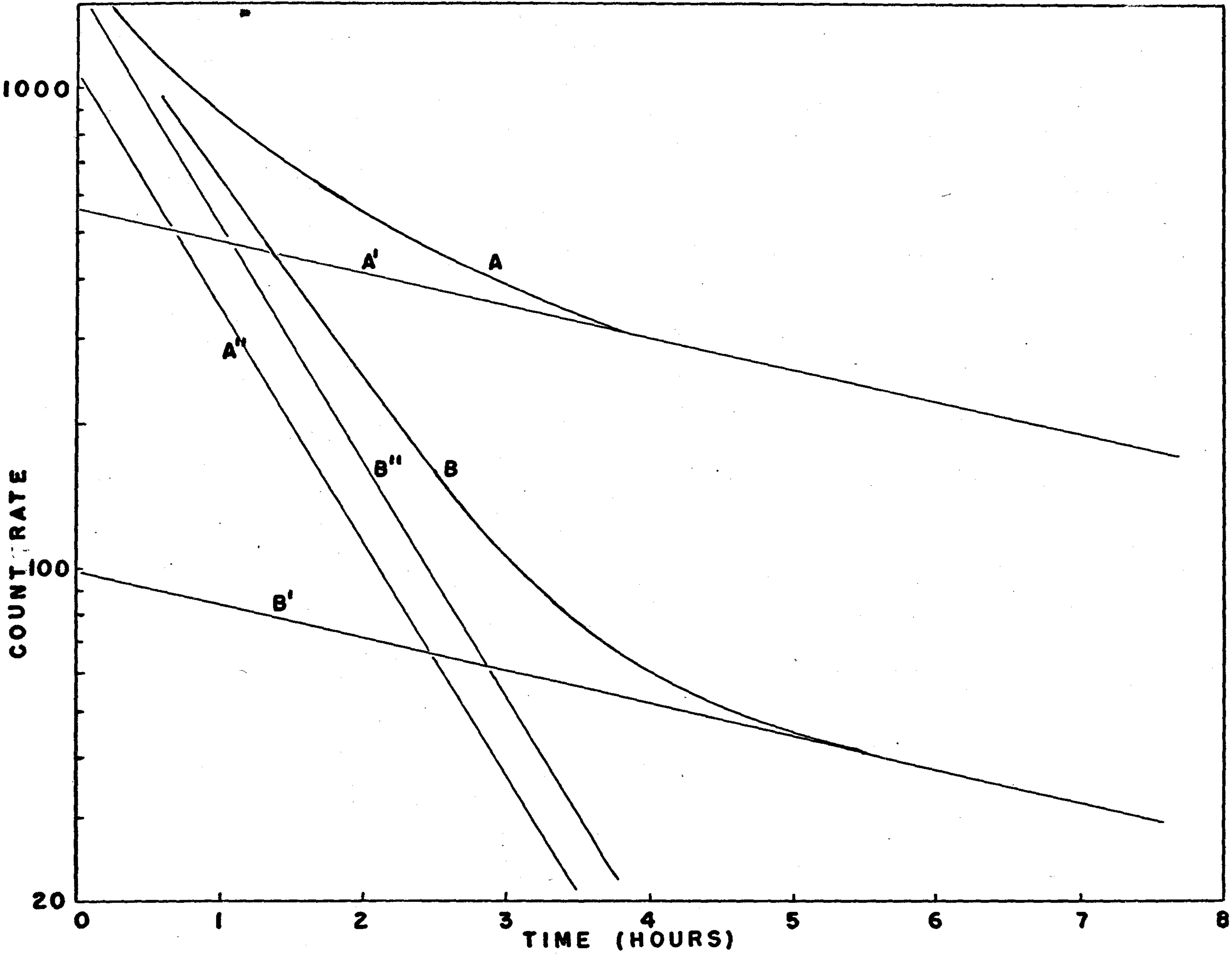


FIGURE 18. DETERMINATION OF ENRICHMENT. A. Total activity in electrodeposit B. Total activity in solution sample. A', B'. 4.5 hr. Br^{80m} A'', B''. 38m Cl^{38}. 20 min electrolysis at 20 ma/cm^2, 1.81 x 10^{-4}M cystine.

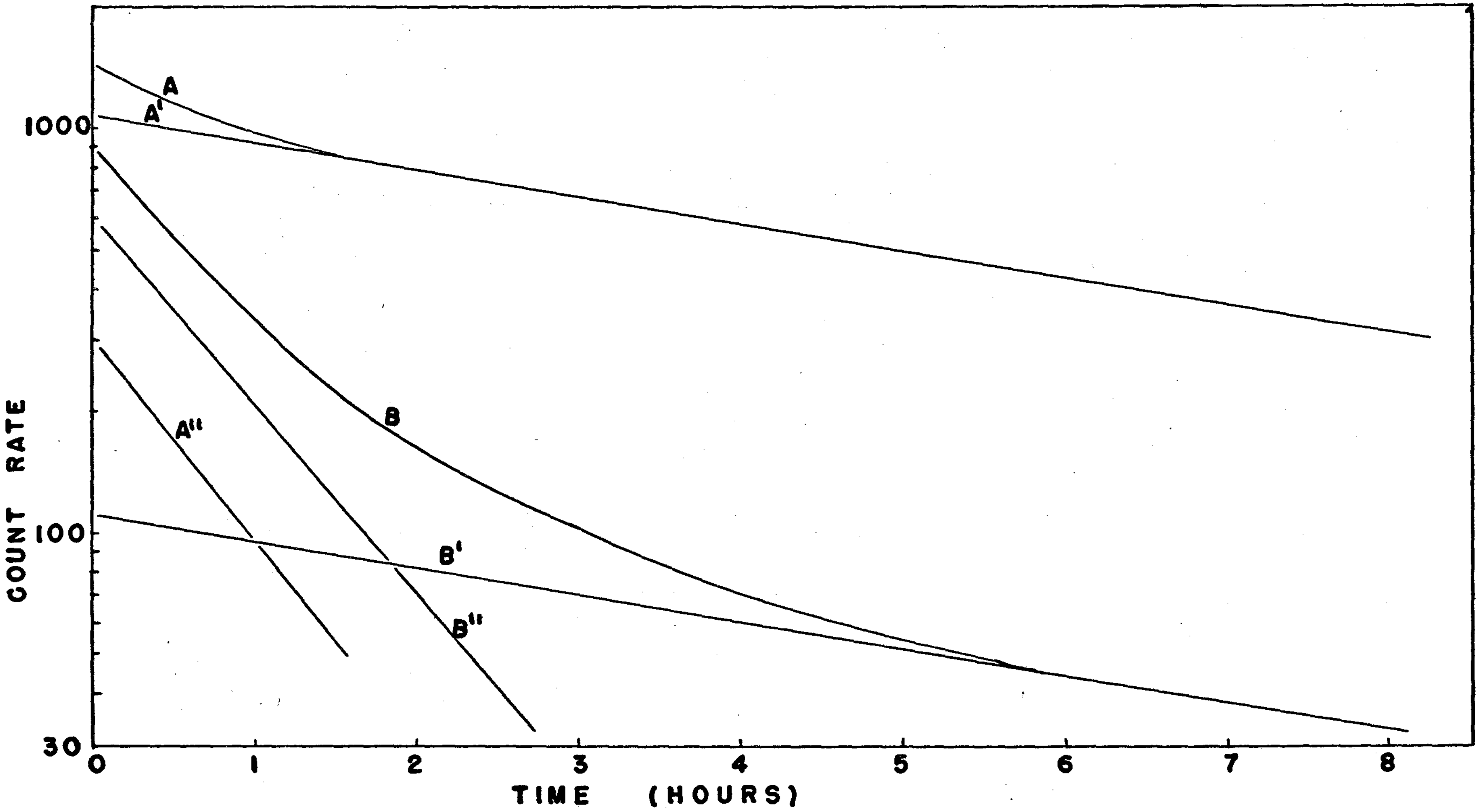


Figure 19. DETERMINATION OF ENRICHMENT. A. Electrodeposit. B. Solution. A',B' 4.5 hr Br^{80m} A'',B'' 38 min Cl^{38}. 1 hr. electrolysis at 4 ma/cm^2, 1.40×10^{-4} M cystine.

TABLE II: ENRICHMENT EXPERIMENTS

Experiment	Surface	Solution	Details	Relative Enrichment (Br^-/Cl^-)
Adsorption	cystine prepared	standard	5 min. immersion	1.4
Adsorption	standard	standard	20 min. immersion	8.9
Electrodeposition	-	standard plus cystine	20 min. at 20 ma/cm^2	8.9
Electrodeposition	-	standard	20 min. at 20 ma/cm^2	25
Electrodeposition	-	standard plus cystine	60 min. at 20 ma/cm^2	23
Electrodeposition	-	standard	20 min. at 4 ma/cm^2	37

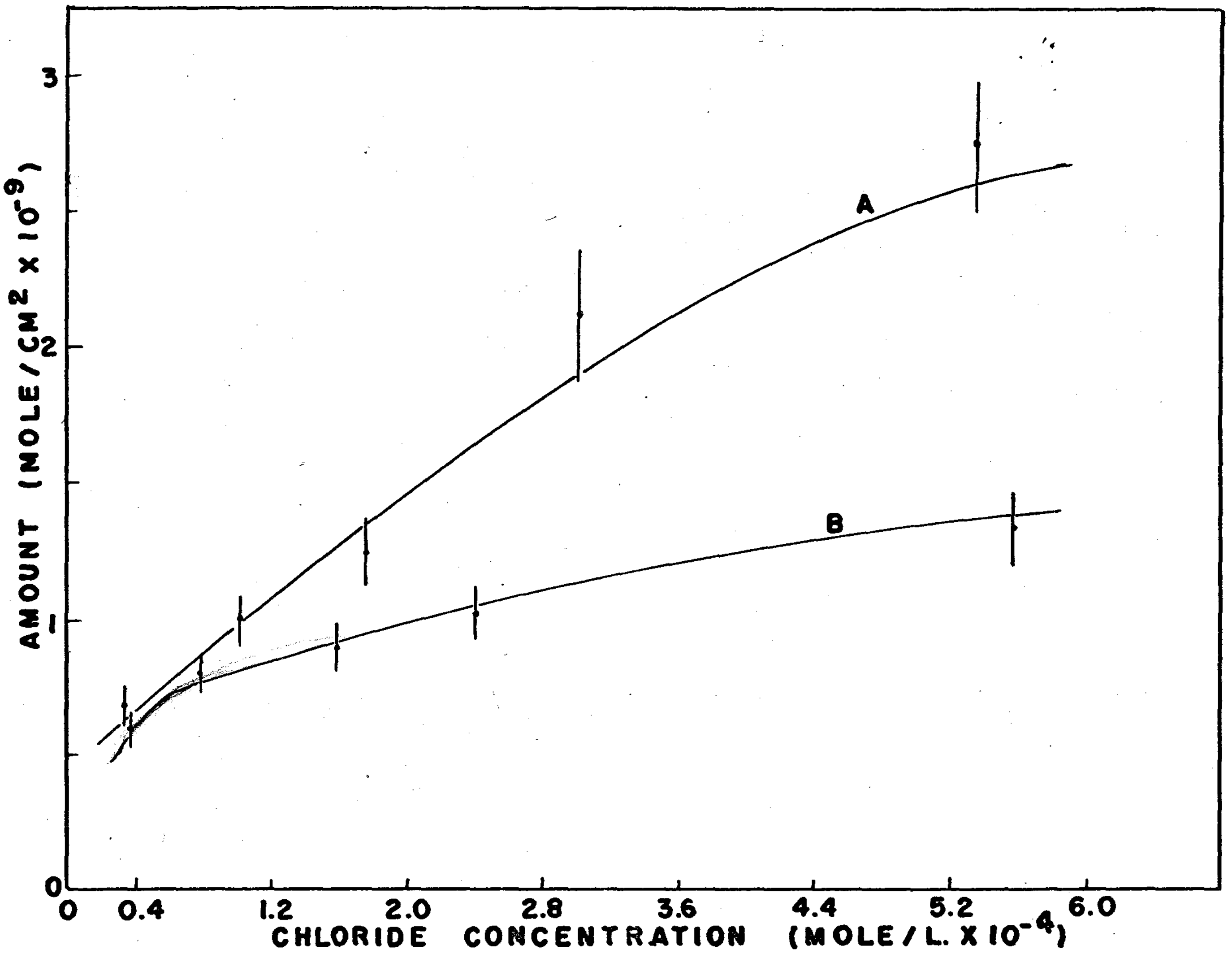


Figure 20. AMOUNT OF CHLORIDE INCORPORATED AT DIFFERENT TEMPERATURES A. 0°C B. 25°C

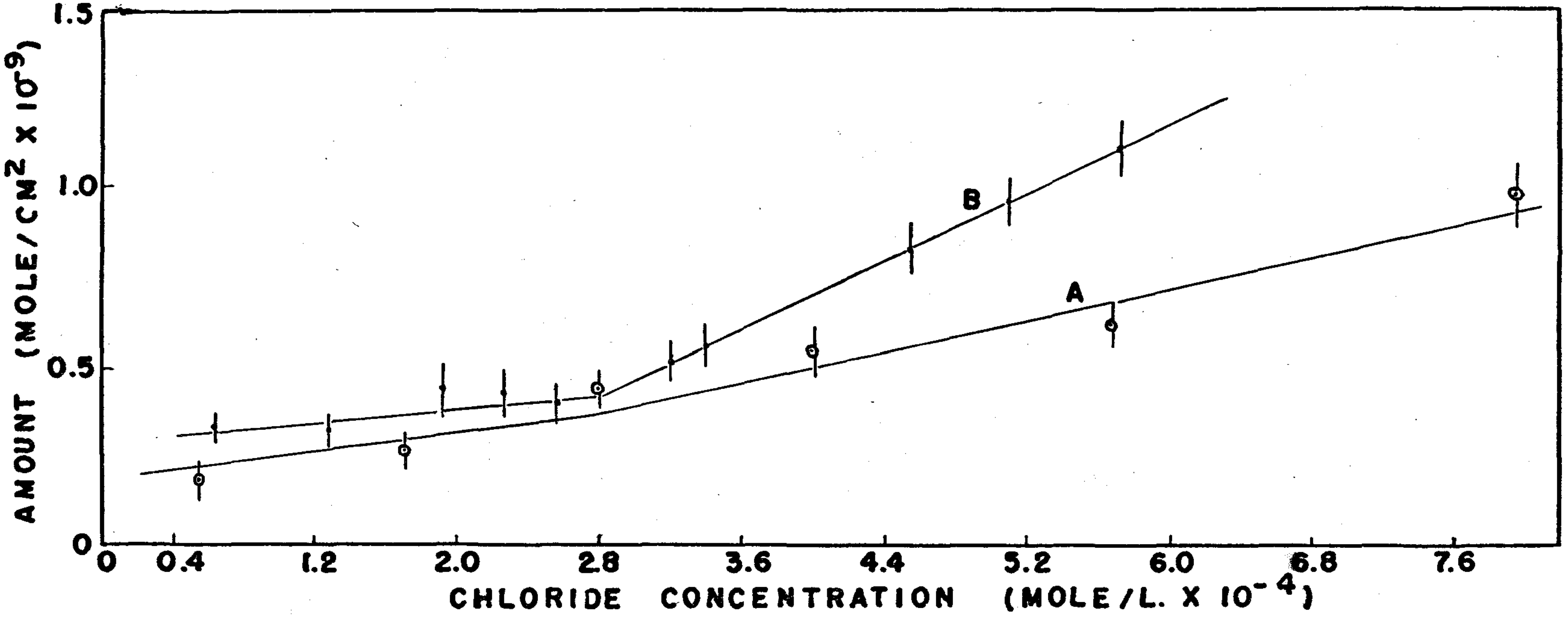


Figure 21. AMOUNT OF CHLORIDE ADSORBED ON THE STANDARD COPPER SURFACE A. 0°C B. 25°C

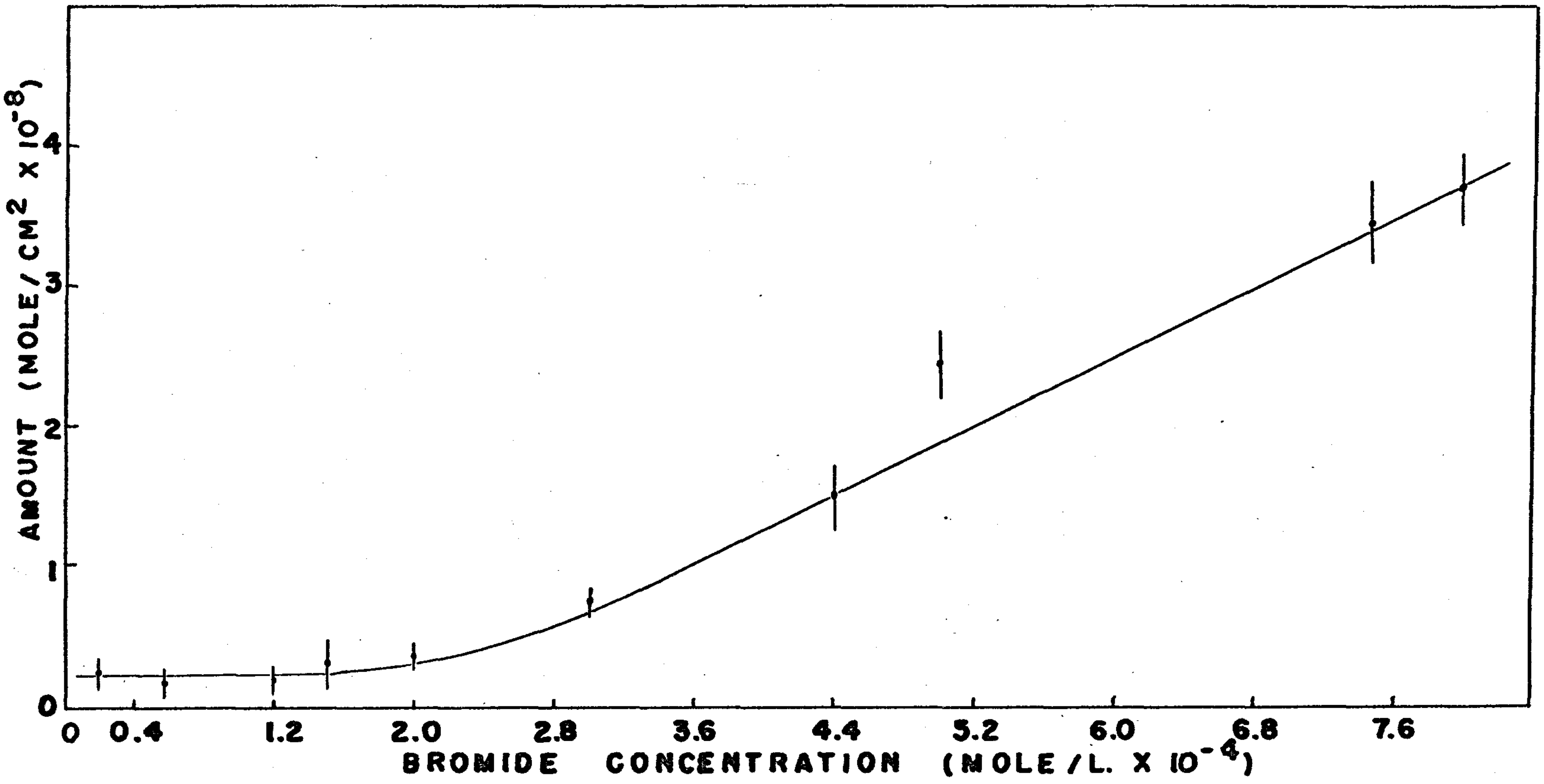


Figure 22. AMOUNT OF BROMIDE ADSORBED ON THE STANDARD COPPER SURFACE

solution from which the copper was electroplated contained 21 mg. cystine in 200 ml. electrolytic solution. The amount of halide adsorbed on the surface is shown in figure 23. It may be seen that the amount of chloride adsorbed on the surface was much greater for this type of surface.

c. Adsorption from distilled water.

The amount of bromine adsorbed on a standard copper surface is shown in figure 24. Reproducibility was significantly poorer during this experiment. It was considerably better when the solution was strongly acid. The difference was attributed to the formation of oxides on the surface in contact with the distilled water. It may be seen that the amount of bromine adsorbed in the plateau region was the same within experimental error for either distilled water or standard solution at low halide concentrations.

d. Adsorption from electrolytic solution containing cystine.

It has been shown (34) that thiourea adsorbs onto a crystal surface from an aqueous copper solution. Cystine is very similar chemically to thiourea, hence it may be assumed that it also adsorbs onto the copper surface. The question to be investigated was "Does the organic additive prevent adsorption of the halides ?". The data are given in figure 25. It may be seen that the amount of halide adsorbed was reduced to about one half by the presence of cystine in the solution.

e. Adsorption at 0°C.

The amount of chloride adsorbed at 0°C is included in figure 21. It may be seen that there was a small decrease in the amount adsorbed at the lower temperature.

f. Adsorption from a mixture of halides.

The relative amount of chloride and bromide adsorbed onto a copper surface from a mixture of halides in solution is included in Table II,

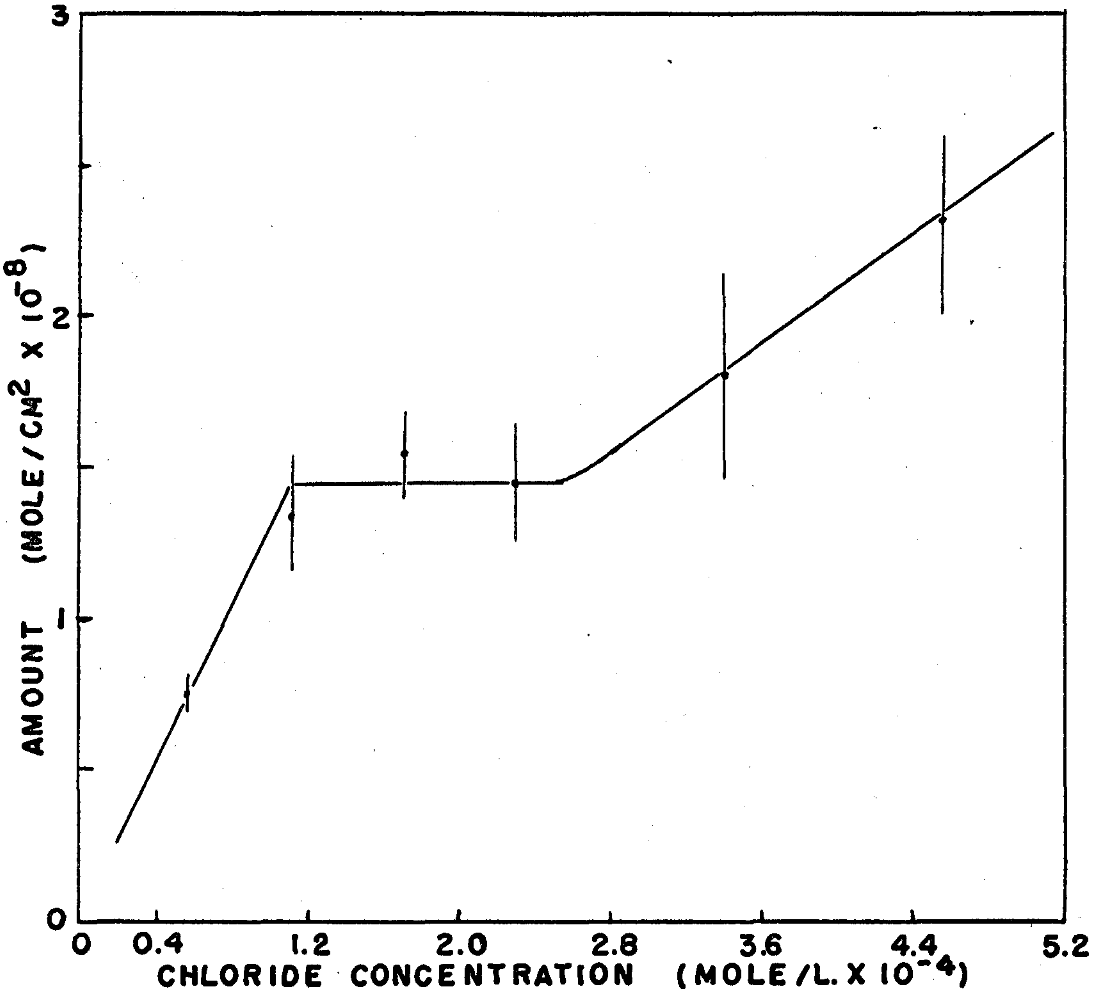


Figure 23. AMOUNT OF CHLORIDE ADSORBED ON A CYSTINE-PREPARED SURFACE

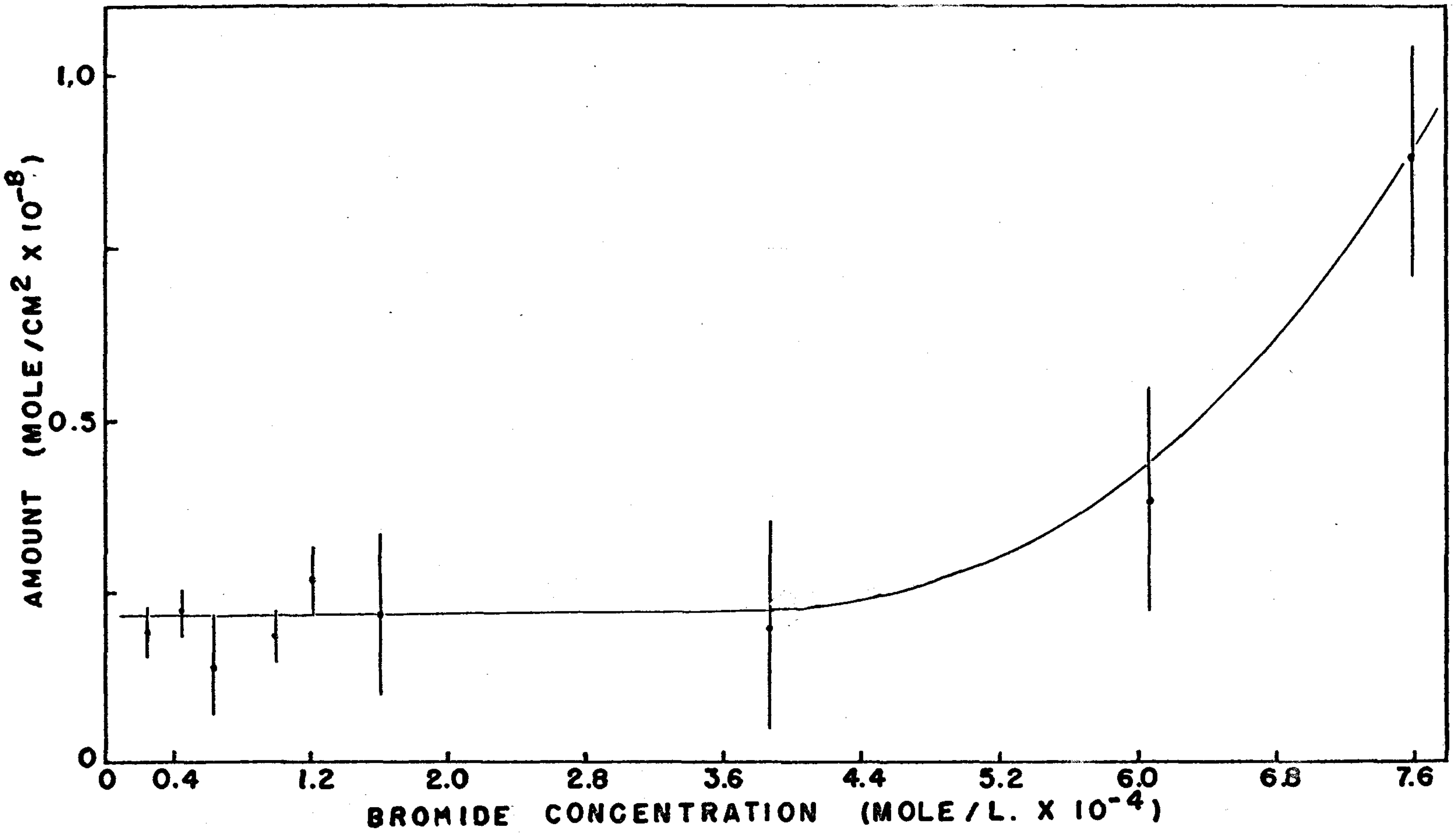


Figure 24. AMOUNT OF BROMIDE ADSORBED FROM DISTILLED WATER ONTO THE STANDARD COPPER SURFACE

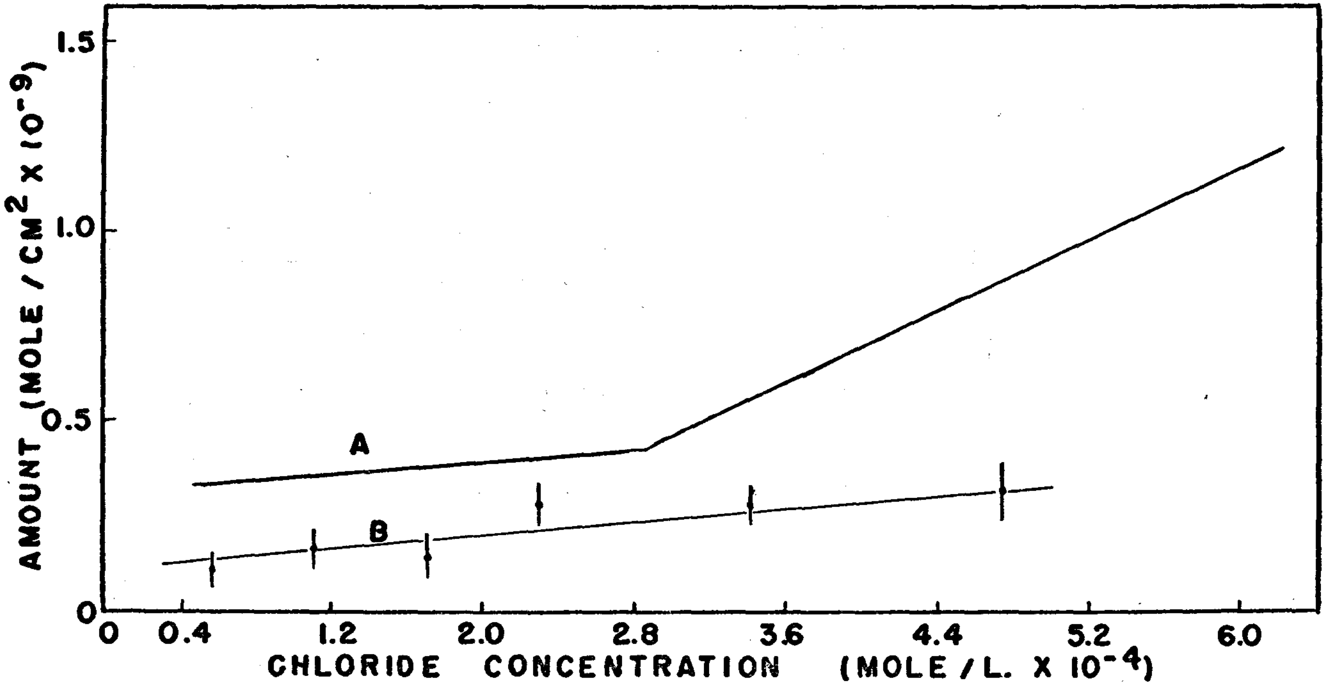


Figure 25. AMOUNT OF CHLORIDE ADSORBED ON THE STANDARD SURFACE A. Standard solution B. 4.38 x 10^{-4}M cystine

page 57 . The solution was 2.2 x 10^{-4} molar in HCl and 1.0 x 10^{-4} molar in HBr. It is evident that for a 5 minute immersion there was a slight preference for bromine over chlorine and that for a 20 minute immersion there was a distinct preference for the bromine. It is important in interpreting these results to recall that the copper atoms in the metal maintain a dynamic equilibrium with copper ions in solution. The preference noted may not be the result of direct adsorption, but rather the result of selection by this exchange current.

Polarization Studies

Almost all of the work that has been done on the mechanism of electrodeposition has been devoted to studies and interpretation of polarization curves. Few studies have been done, however, of the polarization curve, in the presence of the organic additives and halides, within the first 30 seconds. Sukava (49) studied the polarization in the presence of cystine and chloride at 24.5° C. and 20ma/cm^2. Parsons and Winkler (54) have done an extensive study in the presence of gelatin.

a. Preliminary experiments.

Three preliminary polarization experiments were performed.

i. The effect of O_2, He and N_2 bubbling through the electrolytic solution. A nitrogen bubbling chain was set up consisting of a trap containing Fieser's solution to remove oxygen, a concentrated H_2SO_4 trap and three empty traps separating the solutions. The polarization curves of the standard solution and chlorine concentrations at 1.05, 2.10, 6.30, 10.5, 12.6 x 10^{-5} were taken after N_2 had bubbled through the solution for three hours. Fresh solution was placed in the cell. Helium was bubbled through the solution for about one hour. The polarization curve of the standard solution and of several halide solutions was taken. Finally the polarization curve for the standard solution after O_2 was bubbled through it for 30 minutes was taken. No significant change that appeared to be due to the presence of the gases could be detected in any of the curves. It was therefore concluded that having the electrolytic solution exposed to the air did not introduce a serious error. The procedure of helium bubbling through the solution was retained, however, for all subsequent experiments primarily to stir the solution and minimize the effect of convection currents in the cell.

ii. Time between measurements.

The effect of different waiting periods between measurements was determined in the following manner. A solution of 25.4×10^{-5}M cystine in the standard solution was placed in the cell and helium bubbling commenced. Two and one half hours later a picture of the polarization curve was taken. Subsequent pictures of the curve were taken at 100 min.,58 min., 15 min., 10 min., 5 min., 2 min., and 1 min., intervals. Three of the curves are reproduced in figure 26. Curves 1, 2, 3, were taken after waiting periods of 100 min., 5 min., 1 min., respectively. It may be seen that the changes were small even for a 1 minute interval. In practice an interval of about 30 minutes was adopted between all measurements.

iii . Reproducibility.

In general the curves could be readily reproduced to within ± 10 mV. There were two exceptions however. (1) The initial polarization peak for a solution containing cystine but no halide showed considerable variation. (2) The polarization curve for the same solution was noted to give one or the other of two characteristic shapes. The two characteristic curves

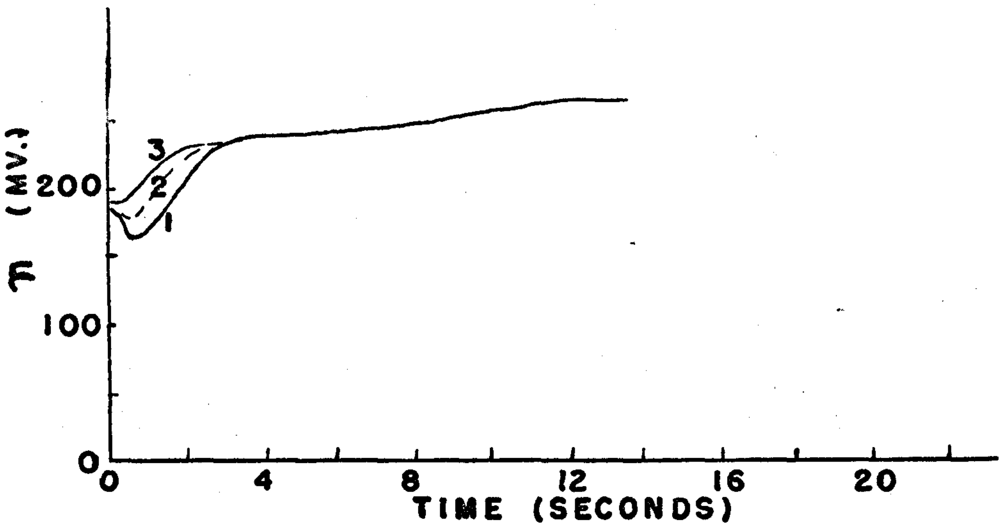


Figure 26. EFFECT OF DIFFERENT WAITING PERIODS 1. 100 min. 2. 5 min. 3. 1 min.

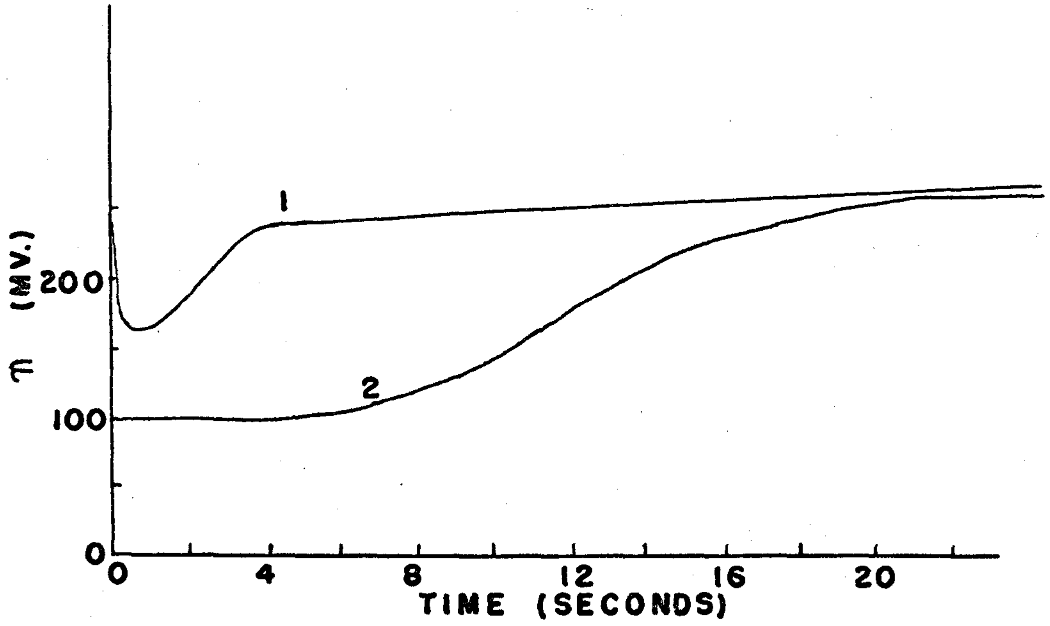


Figure 27. TYPE 1 and TYPE 2 CURVES

are shown in figure 27. The curve labelled 1 was taken on a sample of standard solution containing 2.40 x 10^{-4}M cystine. The solution had been in the cell for half an hour with helium bubbling through it before the polarization curve was taken. The current was on for 40 seconds at a density of 20 ma/cm^2. An hour and three quarters later the polarization curve labelled 2 was taken. In the interval between the two measurements no changes were made in either the solution or the electrode. Helium bubbling was continued during the interval. The curve of type 2 was seen on several occasions, but was never entirely reproducible. Switching the current on for the third and fourth curves showed a curve similar to type 1 minus the initial polarization peak. It may be noted that curves 1 and 2 were similar following the first twenty seconds.

b. Polarization of the standard solution containing HCl or HBr.

The polarization curves at a current density of 20 ma/cm^2 and a temperature of 25.0° C for the standard solution containing increasing amounts of halide up to 4 x 10^{-4}M are shown in figure 28(a) for HCl and 28(b) for HBr. Examination of the curves shows that the change in polarization upon addition of the halides was small. There was an increase of about 25 mV upon the addition of bromide. There was an even smaller increase upon addition of HCl. The fact that the polarization was 150 mV, some 50 mV higher than others have reported (46) is believed to be due to the difference in crystal structure of the electrodeposit. A smooth platinum backing was used in these experiments, hence the electrodeposited copper had to form its own nucleation centers. Large shiny crystals were produced. Gauvin and Winkler (61) state that a higher polarization is observed with coarsely crystaline deposits. The polarization curves were readily reproducible and the character of the curves reported here have been noted by others

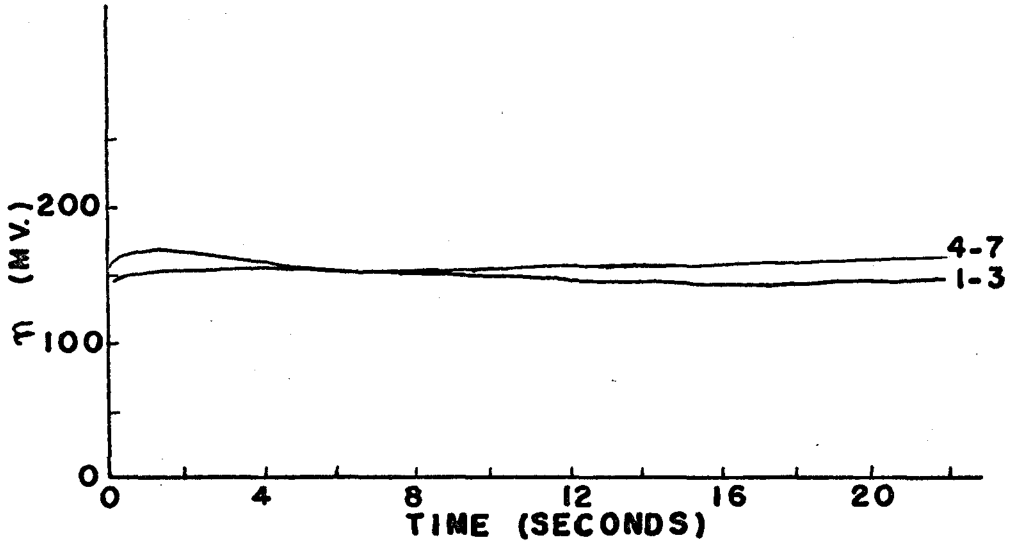


Figure 28(a). CHLORIDE IN STANDARD SOLUTION
1. No chloride 3. 2.10×10^{-5}M HCl
4. 6.32×10^{-5}M HCl 7. 31.6×10^{-5}M HCl
current density 20 ma/cm^2

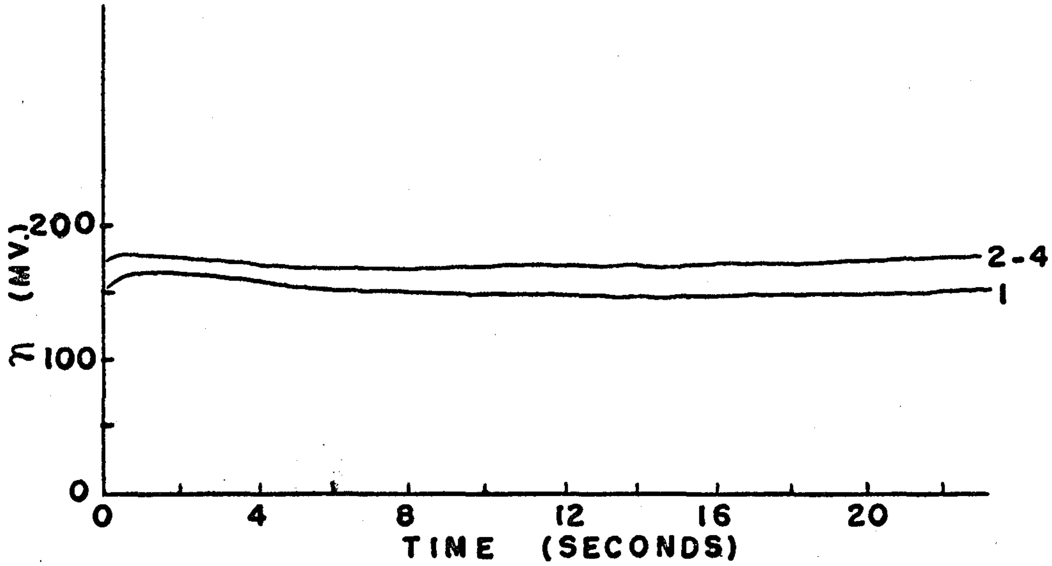


Figure 28(b) BROMIDE IN STANDARD SOLUTION
1. No bromide 2. 4.17×10^{-5}M Br
4. 20.9×10^{-5}M HBr
current density 20 ma/cm^2

(46).

No attempt was made to measure the polarization at shorter time intervals except for two or three experiments. The electrical circuit as used in these experiments was not suitable for short time measurements. It would be necessary to have a constant current source with a much faster rise time than the battery and to replace the mechanical on-off switch and the meters by equipment with a much faster response time.

(c) Polarization in the presence of cystine.

The addition of cystine to the electrolytic solution caused a considerable increase in the polarization. The addition of halide to this solution produced very interesting effects. The initial polarization curves for a standard solution containing 2.40 c 10^{-4}M cystine and increasing amounts of HCl are shown in figure 29(a) and the curves for a solution containing 2.78 x 10^{-4}M cystine plus various amounts of HBr are shown in figure 29(b). The interesting features here are four. (1) Both halides were strong depolarizing agents in the presence of cystine. It may be seen that 2.0 x 10^{-4} moles/liter HCl decreased the polarization by 150 mV. The depolarizing effect of HBr was not as great but still was considerable. The curve in figure 29(b) for no bromide was low and was not reproducible. The curve 1 in figure 29(a) was typical for the halide free solution. (2) Another feature of interest was the initial polarization. It may be seen that for chloride concentrations 8 - 20 x 10^{-5}M the initial polarization was 55 mV. which was lower than for the standard solution containing no organic additive. The same initial polarization was observed for bromide concentrations 4 x 10^{-5} - 2.5 x 10^{-4}M. It was then observed that the initial polarization increased upon further addition of HBr. Only a few of the polarization measurements taken are reproduced here. A continuous

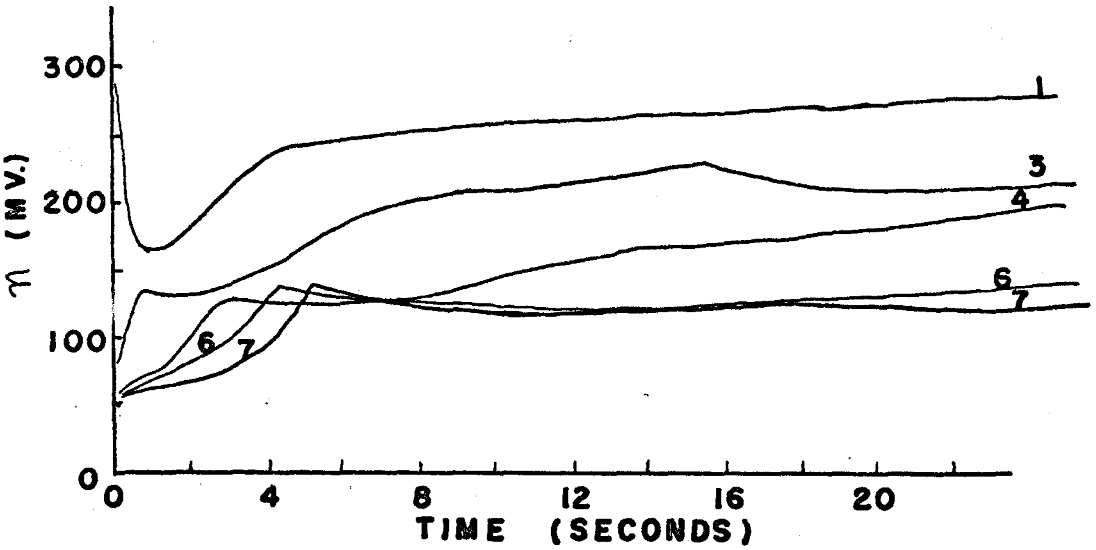


Figure 29(a). CHLORIDE IN 2.40 x 10^{-4} CYSTINE
1. No chloride 3. 4.09 x 10^{-5}M HCl
4. 8.10 x 10^{-5}M HCl 6. 16.4 x 10^{-5}M HCl.
7. 20.4 x 10^{-5}M HCl. current density 20 ma/cm^2

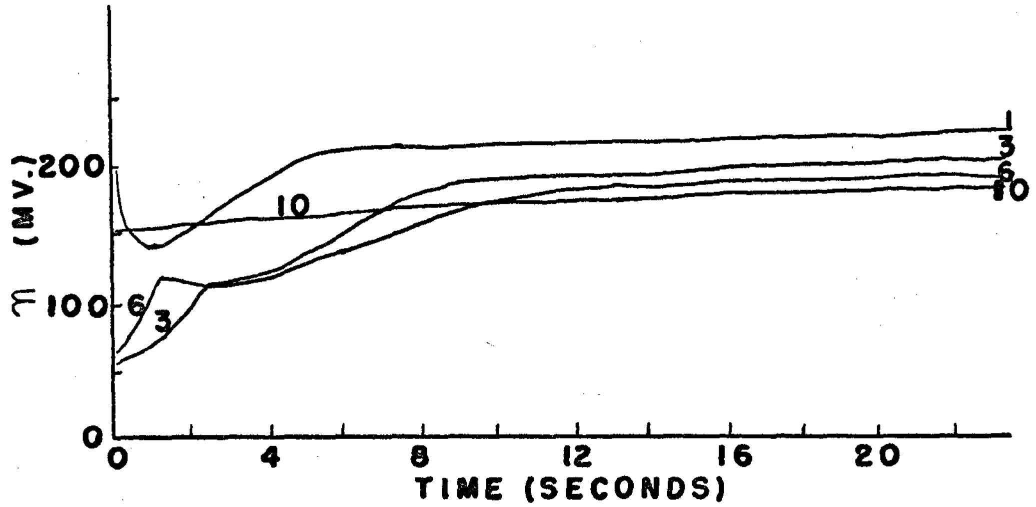


Figure 29(b). BROMIDE IN 2.78 x 10^{-4}M CYSTINE
1. No bromide 3. 4.10 x 10^{-5}M HBr
6. 8.38 x 10^{-5}M HBr 10. 41.9 x 10^{-5} HBr
current density 20 ma/cm^2

transition was observed. (3) A third feature of interest was that it was possible with HCl to lower the polarization below that for a solution containing no organic additive. With HBr it was possible only to decrease the polarization to that of the additive-free solution. (4) The fourth feature of interest is the peak in each of the curves that occurred within a few seconds of the start of electrolysis. This peak was seen to move out to longer times with increasing halide concentration. With HBr only it was observed to move to shorter times and finally disappear at even higher concentrations.

(d) Polarization at different current densities.

Polarization curves at 4 ma/cm^2 for the standard solution plus cystine are shown in figure 30(a) for HCl and 30 (b) for HBr. The reproducibility at this lower current was not as good as at the higher current densities. The shape of the curves was entirely different from those at 20ma/cm^2. There was no indication of a common initial polarization for the HCl curves. The HBr curves did not indicate an increasing initial polarization above 2.5 x 10^{-4} moles/liter. In general the appearance of the curves indicated a slowing down and smoothing out of the features noticed at higher current densities. In figure 29 (a), curve 2 is the polarization of the standard solution plus cystine taken 20 minutes after curve 1.

Polarization curves at 40 ma/cm^2 are shown in figure 31(a) for HCl and 31(b) for HBr. Only a few of the curves measured are shown. The depolarizing effect of the halides is evident. There were no peaks in the curves as had been seen at 20 ma/cm^2. The increase in the initial polarization became evident at 17 x 10^{-5}M HBr which was lower than the 25 x 10^{-5}M

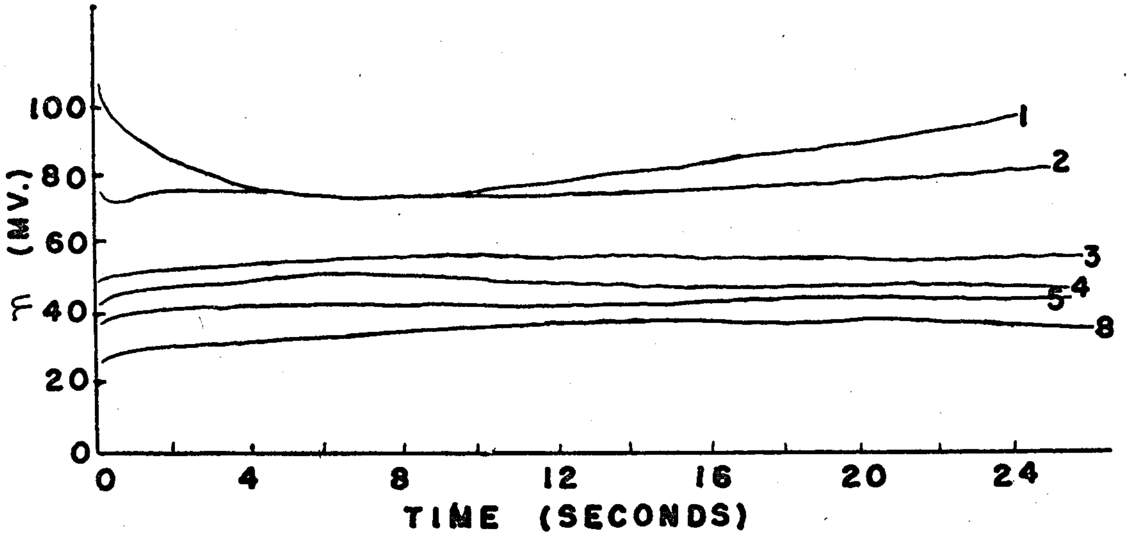


Figure 30(a) CHLORIDE IN 2.41 x 10^{-4}M CYSTINE
1. and 2. No chloride 3. 4.58 x 10^{-5}M HCl
4. 9.15 x 10^{-5}M HCl 5. 18.3 x 10^{-5}M HCl
8. 68.6 x 10^{-5}M HCl. current density 4 ma/cm^2

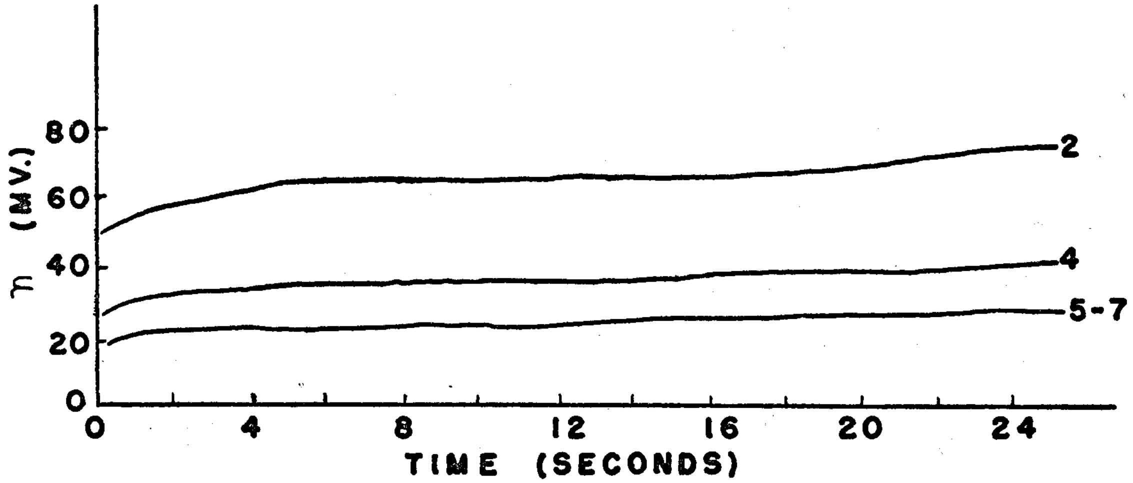


Figure 30(b) BROMIDE IN 2.65 x 10^{-4}M CYSTINE
2. No bromide 4. 4.14 x 10^{-5}M HBr
5. 12.4 x 10^{-5}M HBr 7. 28.9 x 10^{-5} HBr.
current density 4 ma/cm^2

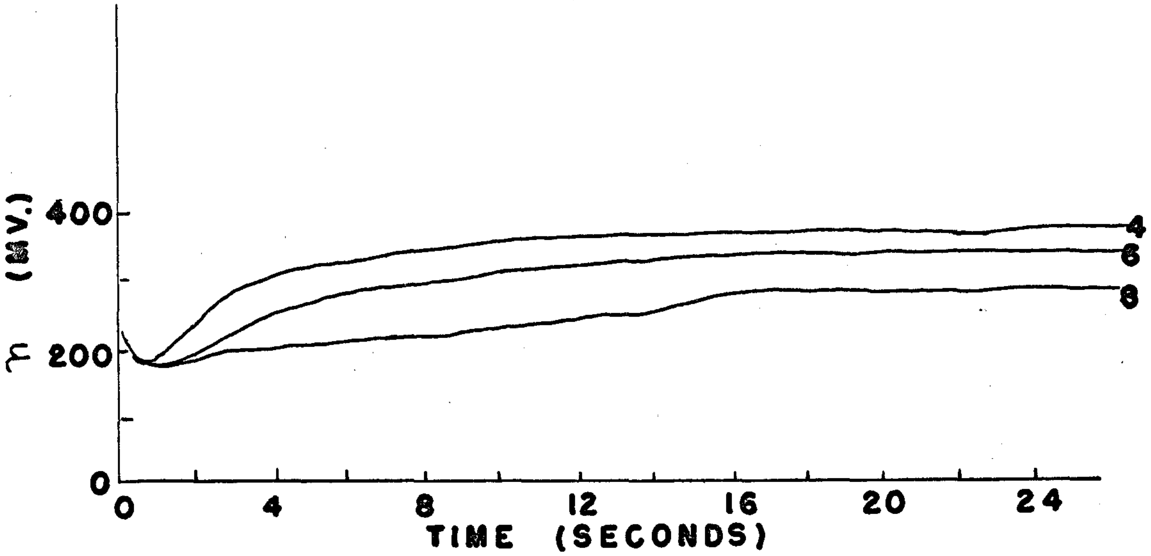


Figure 31(a). CHLORIDE IN 2.52×10^{-4}M CYSTINE
4. 4.65×10^{-5}M HCl 6. 18.6×10^{-5}M HCl
8. 47.0×10^{-5}M HCl. current density 40 ma/cm^2

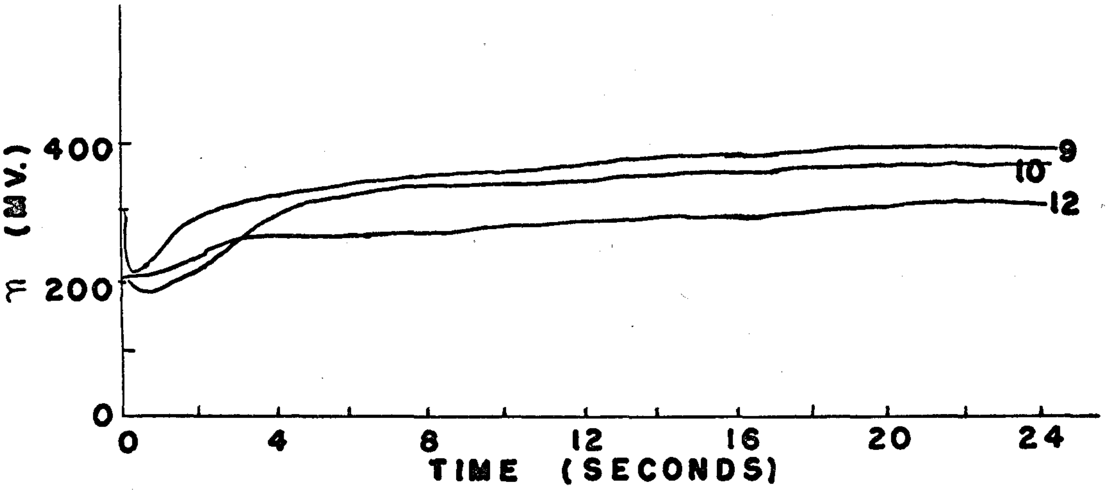


Figure 31(b) BROMIDE IN 2.56×10^{-4}M CYSTINE
9. No bromide 10. 4.30×10^{-5}M HBr
12. 17.2×10^{-5}M HBr. current density 40 ma/cm^2

HBr observed at 20 ma/cm^2.

(e) Polarization at 0°C.

The polarization curves for standard solution containing cystine and HCl were measured at 0°C. The cell was completely immersed in an ice bath for these experiments. The curves are shown in figure 32. The current density was 20 ma/cm^2. It may be seen that the polarization was much greater at the lower temperature and also that the depolarizing effect of the halides was increased.

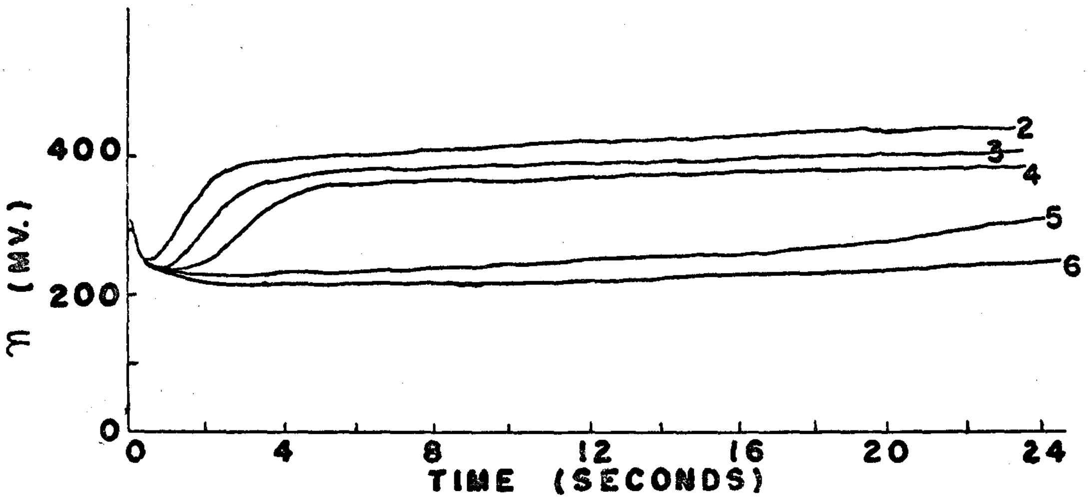


Figure 32. CHLORIDE IN 2.41 x 10^{-4}M CYSTINE
2. No chloride 3. 4.58 x 10^{-5}M HCl 4. 9.15 x 10^{-5}M HCl
5. 27.5 x 10^{-5}M HCl 6. 45.8 x 10^{-5}M HCl. Temperature 0°C.

IV DISCUSSION

In this chapter an hypothesis composed of four main sections is proposed to account for the observed data. When the work described in this Thesis was first undertaken, it was expected that the results would give direct confirmation of the cuprous ion intermediate in the electrodeposition of copper. By using low halide concentrations it was felt that the small perturbation on the system caused by the presence of the halides would be insignificant. However, the presence of an adsorbed layer of halide on the surface of the copper metal proved that the perturbation could not be considered small. Since the adsorbed layer probably has a thickness of only a few angstroms it is evident that halide concentrations at the surface may be very large indeed. It is quite conceivable that the presence of the halides could markedly change the mechanism of the reduction of the cupric ion. When this became evident the research took on broader aspects intended to establish a general outline of the role of the halides as addition agents.

As indicated in the Introduction, previous work in the field of addition agent studies has lead to a variety of hypotheses. To propose a new hypothesis may be considered redundant , but it is necessary that a theory be developed that encompasses the whole of the wide variety of effects observed. The new information contained in this Thesis has suggested an hypothesis broad enough to include a considerable number of observations. Common to the hypotheses previously proposed is the belief that the addition agents act at the surface of the electrode. This is the starting point of the present hypothesis.

Adsorption of both organic and inorganic additives is believed to occur at the copper electrode- aqueous Cu^{++} interface. It is suggested that the halides adsorb on the copper surface. When the copper is made a working cathode, the halides desorb and form a negative layer, the charge of which, is determined by the amount of halide originally adsorbed. This negative layer is considered responsible for a decrease in polarization. Cystine is also adsorbed but it is believed that upon making the copper into a working cathode the cystine is reduced, and the reduction products are incorporated. This leads to an increased energy required for crystallization, which in turn, leads to an increase in cuprous adions. This positive layer causes an increase in polarization. This hypothesis, along with similar views by other workers, will be discussed under the four headings; the adsorbed layer, the interfacial layer, mechanism of incorporation and polarization phenomena.

a. The adsorbed layer.

The study of the adsorbed layer not only gives information about the starting layer but also gives information about the surface characteristics of the electrode. Very little is known about adsorption onto a solid metal in contact with an aqueous solution of its own ions. There are complicating factors. The adsorbate is not a simple atom but is an hydrated ion. There is an electrical field of high intensity and an electrical double layer at the interface. There are other species present that may adsorb onto the metal surface - particularly water molecules. In view of this the data given in this Thesis should not be treated in the same manner as the more common adsorption data for gases.

The shape of the adsorption curves given in figures 21, 22, 23, 24 and 25 suggests that two mechanisms exist for adsorption. In the plateau region occurring at low concentrations, it is believed that chloride is bound to the surface as a result of reaction (1).[1]

$$CuCl^{+} + Cu_{m} \rightleftharpoons Cu_{m}Cl^{-} + Cu^{++} \qquad (1)$$

There is electrostatic repulsion between ions within the bound layer which increases with the degree of saturation. This probably limits the amount of halide adsorbed by reaction (1) and leads in the adsorption curves to a plateau region at less than surface saturation. In fact the estimated degree of surface coverage of chloride is one tenth, and of bromide is one-half, assuming a roughness factor of three for the surface.

A consideration of the relative stability of $CuCl^{+}$ and $Cu_{m}Cl^{-}$ indicates that the former is the more stable because of a greater electrostatic bond energy and hence this reaction is endothermic. A decrease in the amount of halide adsorbed is expected as the temperature is lowered. This was observed. (Figure 21).

A satisfactory explanation of the adsorption curves at higher concentrations has not been achieved. Several models were considered:

Further adsorption of halide could occur by reaction (2).

$$Cu_{m}Cl^{-} + CuCl^{+} \longrightarrow Cu_{m}Cl^{-} - CuCl^{+} \qquad (2)$$

Species of the type $Cu_{m}Cl^{-} - CuCl^{+} - CuCl^{+}$ may also occur. There are two objections to this model. (i) The experimental results show that the amount of adsorbed halide at higher concentrations exceeds that at low concentrations by factors up to twenty and with no apparent limit. (ii) Reaction (2)

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[1] It is shown in Appendix 5 that essentially all the chloride present is complexed as $CuCl^{+}$

is probably exothermic but the increase in adsorption with increase in temperature indicates an endothermic process.

Some halide could be attracted into the positive space charge region of the double layer. It seems unlikely, however, that sufficient halide to explain the experimental observations could be held in this region. An adsorption with similar unexplained characteristics was observed by Ives and Baskin (56) for Fe^{+++} on LiF crystals in contact with a saturated aqueous lithium fluoride solution.

It was observed (Figure 25) that the addition of cystine to the electrolytic solution reduced the amount of adsorbed chloride by one half. Conway and others (57) have measured the amount of quinoline and pyridine adsorbed on a copper surface from an aqueous solution and found it to be in the range $5 - 10 \times 10^{-10}$ moles/cm^2 at a concentration of 10^{-4} molar. Ke, and others (34), have shown that thiourea adsorbs on the copper surface. It is expected that cystine adsorbs on the surface similarly. It is rather surprising therefore that cystine does not completely prevent chloride from adsorbing. It is possible that the halides find sites on the surface that a molecule with greater bulk will find inaccessible. Such sites could be kink sites, the point of crystal growth. Similar ideas have been proposed as a result of the study of dissolution kinetics where it has been found that certain foreign ions act as inhibitors (58,6). The authors have postulated that the foreign ions adsorb on the kink sites and thereby impede dissolution. Studies of the dissolution impedence by ions of different sizes (disc. 58) have shown that, to some extent, size of the ion is important. That is, apparently larger ions cannot adsorb on the kink sites.

It has also been observed (Figure 23) that the amount of chloride adsorbed on a copper surface electrodeposited from a solution containing approximately 10^{-4}M cystine is about forty times greater than the amount of chloride adsorbed on the standard surface (Figure 21). This difference appears to arise solely through changes in the copper surface. Visible differences in the two surfaces are quite noticeable. The increase in adsorption could be the result of hole vacancies at the surface or of atoms in a higher potential energy state than normal. This suggests that the organic additive is entering the copper lattice and disrupting it. The amount of chloride adsorbed on this surface was found to be 1.5×10^{-8} mole/cm^2 in the plateau region (Figure 23). Assuming a roughness factor of three it is seen that the chloride completely covers the surface.

It is possible that the adsorbed chloride layer is not mobile on the surface; it is most likely that the layer becomes mobile as soon as the metal is made a cathode. The mobility of the layer depends upon the surface energy of the metal relative to the energy of desorption. It is the surface energy that changes upon making the metal a cathode.

b. The interfacial layer.

In the previous section, discussion has centered on the copper surface in contact with the electrolytic solution. Attention is now turned to a description of what happens when the metal becomes a working cathode. Two changes are paramount; cupric ions are reduced, and the surface energy is changed by the application of an electric potential to the metal. Under these conditions it appears most improbable that the adsorbed layer of halide may remain specifically adsorbed to the surface. If it did remain specifically adsorbed it would almost certainly be buried in the depths of the electrodeposit.

The studies of the amount of halide incorporated as a function of length of electrolysis combined with the stripping experiments (Figures 15 and 16) conclusively show that there is a layer of halide that remains at the surface of the electrodeposit. This layer moves outwards as the surface grows. Evidence that this layer is not the same as the adsorbed layer discussed in the previous section is seen in the study of the temperature effect on the amount of halide incorporated and on the amount of halide adsorbed. It was found that the amount of incorporated halide increased at lower temperatures whereas the amount adsorbed decreased (Figures 20 and 21). An explanation has already been given for the decrease in adsorption. It is suggested that the increase in incorporation is the result of a chemical process that has a positive heat of reaction. This process is described in the next few paragraphs.

It is assumed that the cupric ion reduction goes through a cuprous ion intermediate as explained in the Introduction. There are two possible mechanisms. In one case the cupric ion in the outer Helmholtz layer undergoes an electronic adjustment in its solvent sheath until the electronic energy level is the same as the Fermi level in the metal. When this occurs electron tunneling takes place which gives rise to a cuprous ion in the outer Helmholtz layer. The cuprous ion is then transferred to the metal surface where it is further reduced and incorporated. This mechanism, however, suggests that the cuprous ion transfer mechanism could be slow enough to be rate determining. All evidence to the present suggests that the reaction between the cuprous ion and metal is very fast. In view of this the second possibility is suggested. Here the cupric ion undergoes transfer to the surface where it forms an adion probably with a +1 charge. As shown in the Introduction it is unlikely that transfer will take place to the growth site. The ion transfers to a plane site where it retains most of its solvent sheath. The adion is mobile and moves to the growth site, at the same time gradually losing its solvent sheath and its charge. It is postulated that a cuprous adion may combine with a chloride ion in the interfacial layer. The cuprous chloride then precipitates and is incorporated. Because the ions are in a strong electric field the formation of cuprous chloride may be a slow process. At low current densities the electric field at the surface of the electrode is not as great as at higher current densities. The probability of formation of cuprous chloride will, therefore, be greater at the low current densities and more halide will be incorporated. At low halide concentrations an increase in the amount of halide incorporated was observed as the current density decreased (Figure 17).

The amount of chloride in the surface layer of the electrodeposit may be determined by plotting the amount "incorporated" at two different times of electrolysis and extrapolating to zero time. This has been done in Figure 34 for several different chloride concentrations. A common intercept of approximately 5×10^{-10} mole/cm^2 is observed. Reference to the curve - Figure 21 - giving the amount of chloride adsorbed shows that the adsorbed layer saturates at 4×10^{-10} mole/cm^2. The agreement between these values suggests that the surface layer of halide saturates. If $(5 \pm 1) \times 10^{-10}$ mole/cm^2 is subtracted from the curves given in the experimental chapter for the amount of chloride incorporated after 12 minutes electrolysis and after 30 minutes electrolysis, the data presented in Figure 35 are obtained. As expected straight lines are found. The ratios of the slopes of these lines is 2.7 ; the ratio of the time of electrolysis for the two sets of data is 2.5 which is in agreement with the conclusion

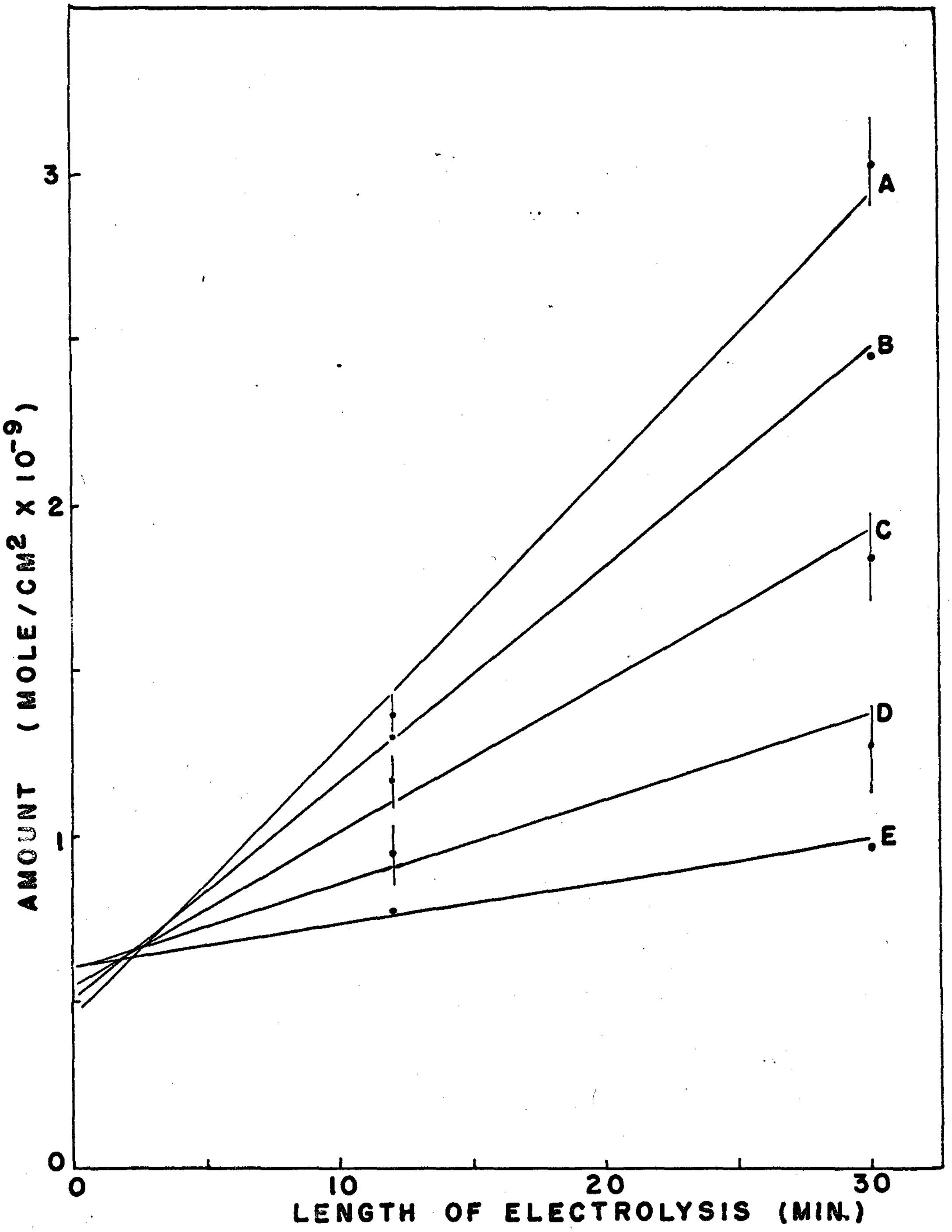


Figure 34. AMOUNT OF CHLORIDE INCORPORATED VS. TIME AT VARIOUS CHLORIDE CONCENTRATIONS.

A. 4.8×10^{-4}M HCl B. 4.0×10^{-4}HCl C. 3.2×10^{-4}M HCl D. 2.0×10^{-4}M HCl E. 1.0×10^{-4}M HCl

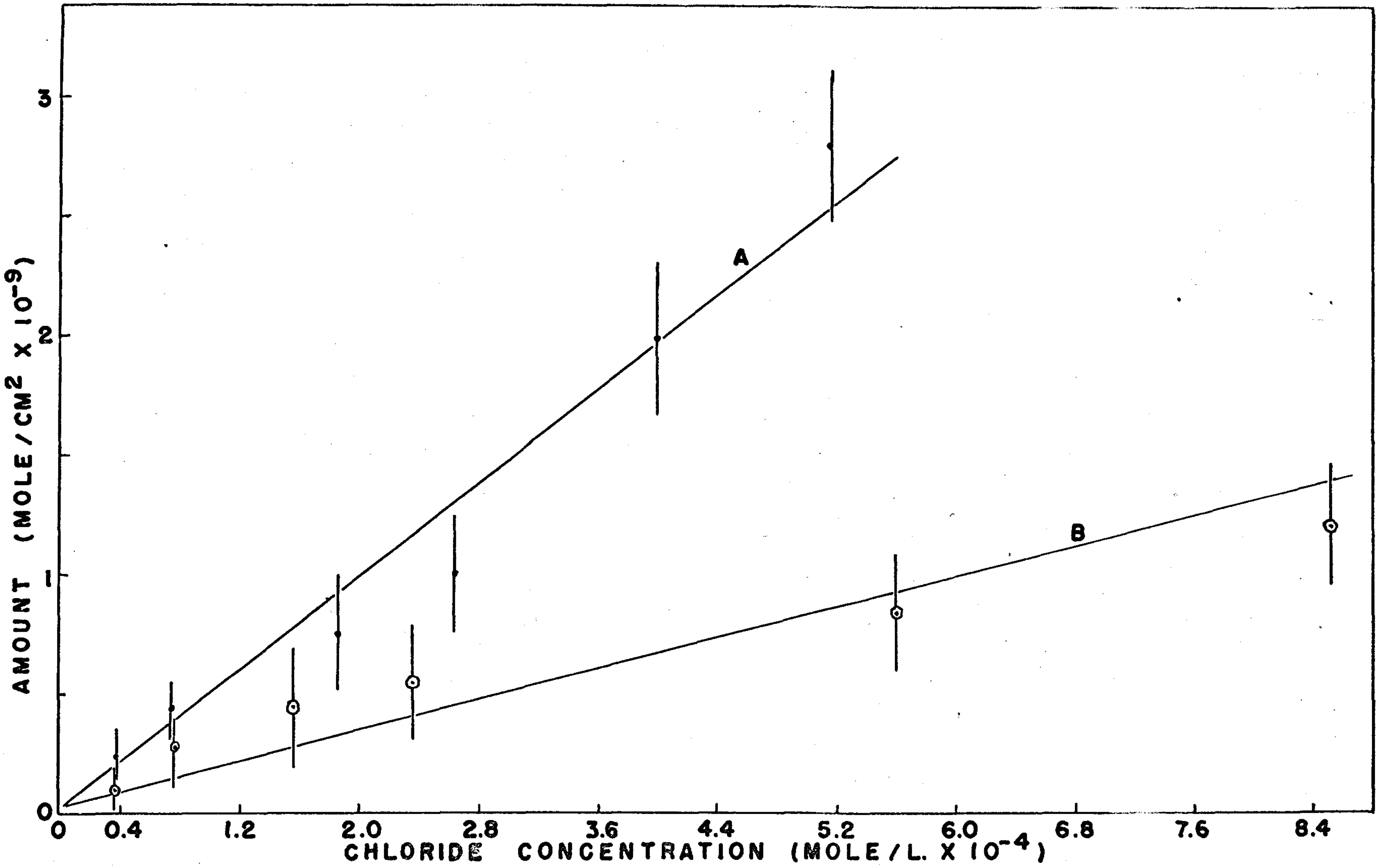


Figure 35. CHLORIDE INCORPORATED VS. CHLORIDE CONCENTRATION . A. 30 min. B. 12 min. electrolysis at 20 ma/cm^2

that there is a layer of chloride at the surface of a deposit containing a uniform amount of chloride.

It is interesting to note that the amount of halide in the surface layer of the electrodeposit may be predicted. Examination of the curve for the amount of halide adsorbed on a copper surface prepared from a solution containing cystine (Figure 23) indicates an adsorbed layer of 1.4×10^{-8} mole Cl^-/cm^2. The stripping experiment on an electrodeposit prepared from a similar solution (Figure 16) showed a surface layer of 1.35×10^{-8} mole Cl^-/cm^2.

Cupric ions are continually removed from the solution at the working cathode. From an examination of the stability constants for the complex cupric halides in aqueous solution, it is concluded that at the concentrations used one halide ion is complexed with one cupric ion (see Appendix 5). It must be recognized that halides are continually brought to the cathode surface in conjunction with cupric ions. The fact that the halide layer saturates must require that the incoming halides are either incorporated or accumulate outside the saturated layer. It may be calculated that at a current density of 20 ma/cm^2 and a halide concentration in the bulk of 1×10^{-4}M, that 2×10^{-11} $mole/cm^2$ are brought to the surface per second by this process. In 12 minutes 1.4×10^{-8} $mole/cm^2$ are brought in. The amount incorporated is a small fraction of this, so it must be concluded that the excess halide passes back into the solution. It may be seen that there is enough halide passed back into the solution to saturate the cupric ions in the $Cu\,Cl_4^=$ complex to a depth of approximately 1 Å per second. At this rate it would take about five years before a layer 1 cm deep would be saturated. Convincing evidence that the layer does not change as electrolysis proceeds is found in the analysis of the polarization curve for there is no change with time that can be attributed to changes in the inner Helmholtz layer. This will be discussed further in the last section of this chapter.

The amount of chloride in the inner Helmholtz layer apparently is determined by the surface with which it is in contact. The study of the amount of halide adsorbed on the surface, prepared by electrodeposition from a solution containing an organic additive, shows that this surface adsorbs much more chloride than the standard surface. In addition it is shown that the amount of chloride incorporated is much greater when electrodeposition occurs in the presence of the organic additive (Figure 14). The conclusion is that the organic additive changes the surface structure of the metal and that this new surface gives rise to a greater amount of halides in the inner Helmholtz layer. It has already been shown that the mere presence of cystine in the solution does not change the amount in the adsorbed layer in the same manner as changes in the surface. This conclusion requires that incorporation of the halides does not lead to an appreciable change in the surface structure of the metal.

c. Mechanism of incorporation.

To distinguish between adsorbed and incorporated halides, the exchange properties of the material were investigated. It was found that about 75% of the adsorbed layer would exchange during a 5 minute immersion in non radioactive 0.01M KCl solution. On the other hand the surface layer formed on the electrodeposit did not exchange so readily. This is clearly shown in Figure 16. About 20% of the surface layer exchanged during a 5 minute immersion in 0.01M KCl. Another 24% exchanged during another 5 minute immersion. It appears that the halide in the surface layer of the electrodeposit is held in a form different from that in the adsorbed layer. If it is assumed that the halide in the surface layer of the electrodeposit is held as cuprous halide; the slower rate of exchange of chloride from this layer may be explained by the greater covalent character of CuCl as compared to Cu_nCl^-.

It has been suggested that an equilibrium is established between the halide ions in the inner Helmholtz layer and the copper adions on the surface. Two of the experiments given in this Thesis support this hypothesis. Temperature studies have shown that the amount of halide incorporated increases at lower temperatures but that the amount of halide adsorbed decreases at lower temperatures. The formation of cuprous chloride from hydrated ions is an exothermic reaction ($\Delta H = -6.4$ Kcal/mole (59)) hence lowering the temperature increases the amount of cuprous chloride formed. The formation of CuCl as a preliminary to incorporation is a possible mechanism that explains the increased amount of chloride incorporated at lower temperatures.

The study of the relative amount of each halide incorporated from a mixture of HCl and HBr in the electrolytic solution was particularly informative. As shown in the chapter on experimental results, the preference of bromine over chlorine for incorporation was remarkable. These results seem to rule out the possibility of random trapping. Only a chemical reaction preceding incorporation could give the selectivity noted. The chemical reaction is believed to be the formation of the corresponding cuprous halide. Because cuprous bromide is more insoluble than cuprous chloride it is apparent that bromine will be incorporated before chlorine if the mode of incorporation is the cuprous salt and if both salts can fit equally well into the copper lattice. The interatomic distance in copper metal is 2.34 Å; in both $(CuBr)_n$ and in $(CuCl)_n$ it is 2.25 Å (60). It may be seen, therefore, that the introduction of the cuprous halides into the copper lattice will create some strain but from the standpoint of size, there will be no preference shown for one of the halides over the other.

The study of the role of the organic addition agents upon the amount of chloride incorporated lead to two interesting facts. The amount of halide incorporated was much greater than in the additive-free solution and there was a marked decrease in the amount incorporated at a chloride concentration of about 2.8×10^{-4}M in the bulk solution (Figure 14). It was also noted that at halide concentrations below this value the electroplated surface of the copper had the familiar smooth microcrystaline structure, but above this value the surface appeared to take on the structure obtained from the additive free solution. The increase in the amount incorporated is attributed to two factors; (1) the amount of halide in the interfacial layer is increased when cystine is present in the solution (see page 86) and (2) under the same conditions the concentration of cuprous adions is increased (section d of this chapter). The decrease in the amount of chloride incorporated at concentrations above 2.8×10^{-4}M is believed to be related to the change in crystal structure of the deposit.

The formation of cuprous chloride as an intermediate has been suggested by Gauvin and Winkler (46) from polarization studies. They noted that below 9 mg/liter chloride (2.7×10^{-4}molar) there was no effect on the polarization. Using a value of 0.65×10^{-3} moles/liter as the cuprous ion concentration at the surface of the cathode they concluded that cuprous chloride would not form below a concentration of 2.7×10^{-4} moles chloride per liter. However, as shown, the chloride concentration at the surface of the copper is far different from this value. They also measured the amount of chloride incorporated in large electrodeposits (22.7 gm) and at chloride concentrations above 3×10^{-3} mole/liter. (The deposits used in this work weighed approximately 10^{-2} gm and the halide concentrations used were less than 10^{-3}M). The amount of chloride they found incorporated, measured by the potentiostatic method using the silver-silver chloride electrode, ranged from about 0.04% at 100 mg Cl^-/liter to 0.07% at 400 mg Cl^-/liter. The highest value in the present work -3.3×10^{-9} mole/cm^2 for 30 minute electrolysis at 17 mg/liter - gives a weight ratio of 0.01%. The agreement therefore is encouraging.

e. Polarization results

The study of the adsorbed layer has shown the conditions existing before electrolysis, and the study of the amount of halide incorporated has shown the conditions at the end of the electrolysis. In order to study changes during electrolysis, recourse is made to a study of polarization as a function of time.

Polarization studies of the copper system with various additives in the electrolytic solution have been carried out by several researchers. The most extensive study has been carried out by C. A. Winkler in conjunction with others (46, 48, 49, 54, 61). A full explanation of the polarization curves, however, has not yet been obtained. The curves, particularly in the presence of the organic additives, are evidently complex. With the insight gained from the adsorption and incorporation studies an attempt will be made in this chapter to analyze the curves. Pertinent to the analysis is the requirement that the total polarization may be divided into four parts (a) concentration polarization (b) transfer polarization (c) ohmic or crystallization polarization and (d) "polarization" due to simultaneous reduction of a foreign species. Each of these may be examined in turn.

Concentration Polarization: The reduction of cupric ions at the surface of the cathode leads to a depletion of ions in the outer Helmholtz layer. The change in potential that results from this may be calculated from the Nernst equation. The concentration polarization has been calculated for the present system and found to be almost negligible. The calculation and results are presented in Appendix 4.

Transfer polarization: Where transfer is the rate controlling step in the electrode reaction, the relationship between current density and polarization may be deduced by application of the equilibrium rate theory as explained in the Introduction. This results in an exponential relationship between the current density and the transfer polarization. The equation may be rewritten as shown in the Introduction to give

$$\eta_A = \frac{2}{1-\gamma}\,(k\,T\,\ell n\,i - k\,T\,\ell n\,A + \Delta\,u^{chem})\ .$$

Since everything inside the brackets is a constant for constant current density, our attention is focused on the factor γ which is determined by the sign of the charge on the ions in the inner Helmholtz layer. If anions collect in the inner Helmholtz layer, γ is negative and the polarization drops; if cations collect in the layer, γ is positive and the polarization increases. The filling of the inner Helmholtz layer with ions may be likened to the charging of a capacitor. As is well known the relationship between charge and time for such a system is exponential in nature.

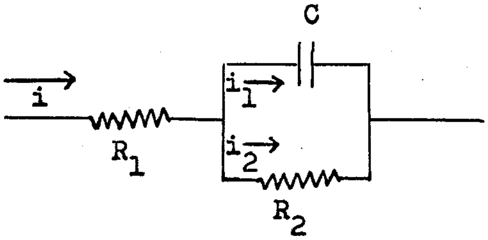
The term $1 - \gamma$ is defined by the equation

$$\psi_+ - \psi_- = (1 - \gamma)\,\Delta\psi_d \qquad .$$

Here $\psi_+ - \psi_-$ is the potential that a reacting ion "sees" as it passes through the double layer. $\Delta\psi_d$ is the measured difference in potential between the electrode and a reference electrode.

The magnitude of the term $1 - \gamma$ cannot, at the present time, be estimated. The manner in which the term changes with time may, however, be determined. It is suggested that, when measuring $\Delta \psi_d$, in effect changes in the difference in potential between A and B in Figure 34(a) are measured. The fact that the concentration polarization is negligible for the system of a vertical electrode means that the charge density Z does not change appreciably with time. Changes in charge density Y caused by accumulation of adions therefore create similar changes in charge density X since overall electrical neutrality must be maintained. Two examples of such changes are shown in Figure 35(b) and (c). As cations collect in the interfacial layer, the charge density X increases and results in an increasing polarization. As anions collect in the interfacial layer, charge density X decreases and a decreasing polarization is observed.

In the next section it will be shown that the presence of cystine leads to an activation energy for incorporation of cuprous adions into the lattice. This means that in the presence of cystine there will be an increase with time in the cuprous adion concentration. An analysis of the change in polarization with time may be made from the following circuit analogue of the double layer:



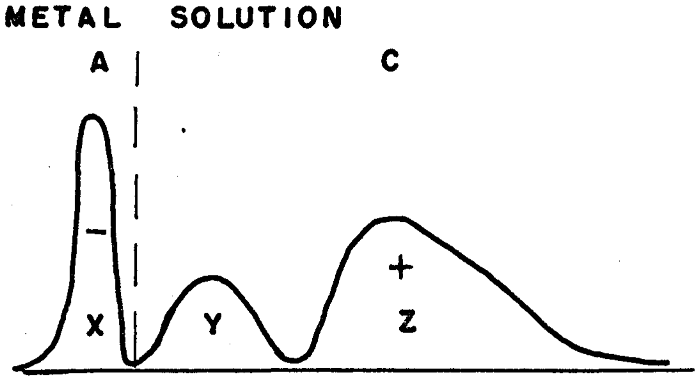


Figure 35(a) STANDARD INTERFACE

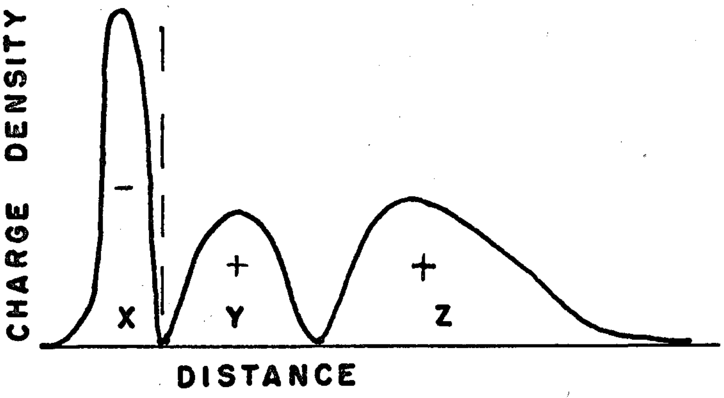


Figure 35(b) CATION ADSORPTION

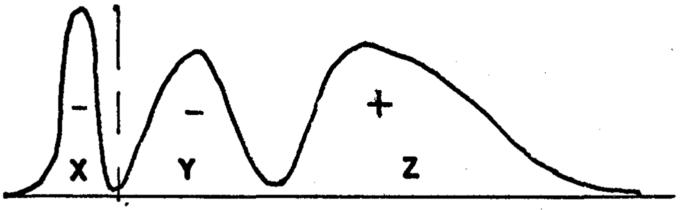


Figure 35(c) ANION ADSORPTION

Here C represents the capacitance due to the presence of a layer of cuprous adions. Because there is also a Faraday current flowing a path through R_2 is included. The resistance R_1 includes the Ohmic polarization. The charge density of one plate of the capacitor is (Appendix 6):

$$\rho = \frac{C}{A} \left(i\, R_2 - i_1\, R_2\, e^{-\frac{t}{CR_2}} \right) .$$

This equation shows that the charge density of the adions increases with time and therefore the polarization should show the same time dependence. A test of this equation is that a plot of log $(\eta_\infty - \eta_t)$ versus time will be a straight line. Such a plot is given in Figure 36 for a polarization curve found for a solution 2.56×10^{-4}M in cystine and 4.30×10^{-4}M in bromide.

Schuldiner and Hoar (62) have suggested that the presence of the organic additive adds a second RC circuit to one already present for the case of no additive. It does not appear to be necessary to introduce a second RC circuit. Their estimate that the time constant of the circuit is about 1000 times greater in the presence of an addition agent does appear to be correct, however. Bockris (12) found the potential for an additive free solution to increase during the first few milliseconds after current was switched on. In this work the potential increase is observed at intervals 1000 times longer.

Ohmic or crystallization polarization: Concentration polarization occurs as a result of a decrease in concentration of the reacting species in the outer Helmholtz layer. Transfer polarization is the result of changes in the energy required to move the reacting ion from the outer Helmholtz layer to the metal surface. The ohmic or crystallization polarization includes terms for all the energy changes from the time the ion reaches the metal to the time it is finally incorporated. Unless crystallization is

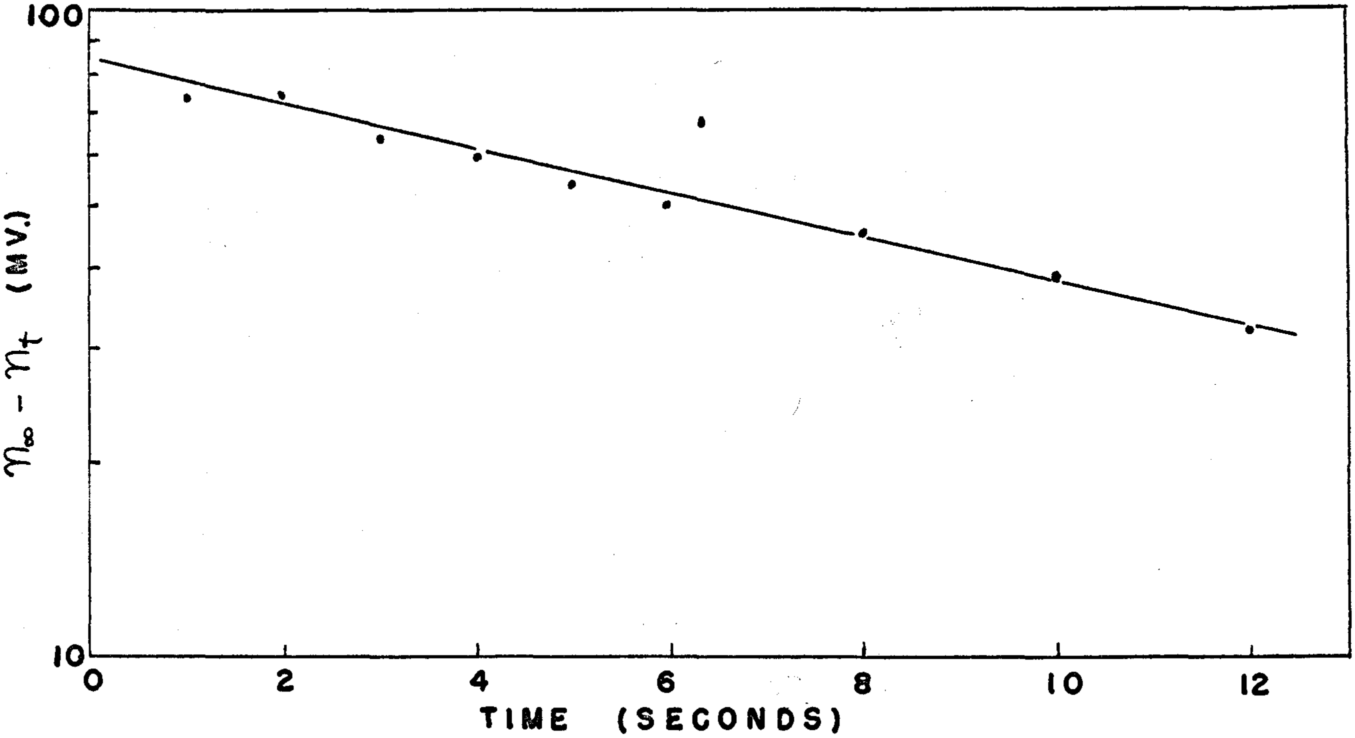


Figure 36 LOG $(\eta_\infty - \eta_t)$ VERSUS TIMES; Solution 2.56 x 10^{-4}M cystine and 4.30 x 10^{-4} Br^-.

activated, ohmic polarization will show a linear dependence with current density. This relationship has been observed and has led to the conclusion that surface diffusion is the rate controlling step for the electrodeposition of copper at low current densities (12). An estimate of the ohmic polarization for the system under discussion may be made by extrapolating from the low current density values included in reference 12. Ohmic polarization values of 12, 15, 18 mV are found by this method for current densities of 4, 20, 40 ma/cm^2 respectively.

In order to explain the increased polarization for a solution containing cystine, it is suggested that cystine is reduced at the cathode and incorporation of the reduction products leads to an activation energy for crystallization of the copper adions. This statement may be tested by a careful measurement for solutions containing additive of the polarization at very low current densities as a function of temperature. The only data available are measurements made by Gauvin and Winkler (61) on a similar electrolytic solution containing gelatine. A polarization of approximately 10 mV was observed for an additive free solution at 50.1° C and 24.8° C. For a solution containing 10 mg gelatine per liter, it was observed that the polarization was 25 mV at 24.8° C and 20 mV at 50.1° C. Since at these low current densities ohmic polarization predominates, it is plausible that the decrease is due to the activation energy of incorporation. D. R. Turner (35) has suggested that several organic addition agents are reduced at the cathode and the reduction products are incorporated. It has also been suggested that the additive initially disrupts the crystal structure by adsorption and then becomes trapped in the open spaces of the lattice along with some electrolyte (63,64). It is known that the weight of the electrodeposit increases when an organic additive is present in the solution.

The presence of cystine in the solution leads to a microcrystalline structure of the electrodeposit. This smaller crystal size would be expected to result in a lower ohmic polarization. The activation energy for incorporation, however, increases the ohmic polarization.

Time dependence of the ohmic polarization: If no time dependent changes in crystal structure of the electrodeposit occur, then the ohmic polarization is constant with time.

A fourth polarization term which is the result of reduction of cystine at the cathode is now considered. It is recognized that use of the word polarization is not correct in this context. The change in potential caused by this phenomenon, however, is added to the three true polarization terms. It is believed that cystine adsorbs on the electrode surface. When the metal is made a cathode the surface is blocked by this compound. The potential of the surface must rise to a value where the adsorbed layer either becomes mobile, is reduced or is incorporated. From an examination of the polarization curves, it is suggested that the cystine is reduced, with the result that during the first second or two an exponentially decreasing potential that is the sum of the reduction potential of the cupric ion and the adsorbed cystine, is observed.

The total polarization of the cathode is the sum of these four terms. This is depicted in Figure 37. Where approximate values are known for the partial polarizations, these are drawn in with dashed lines. Where no ap-

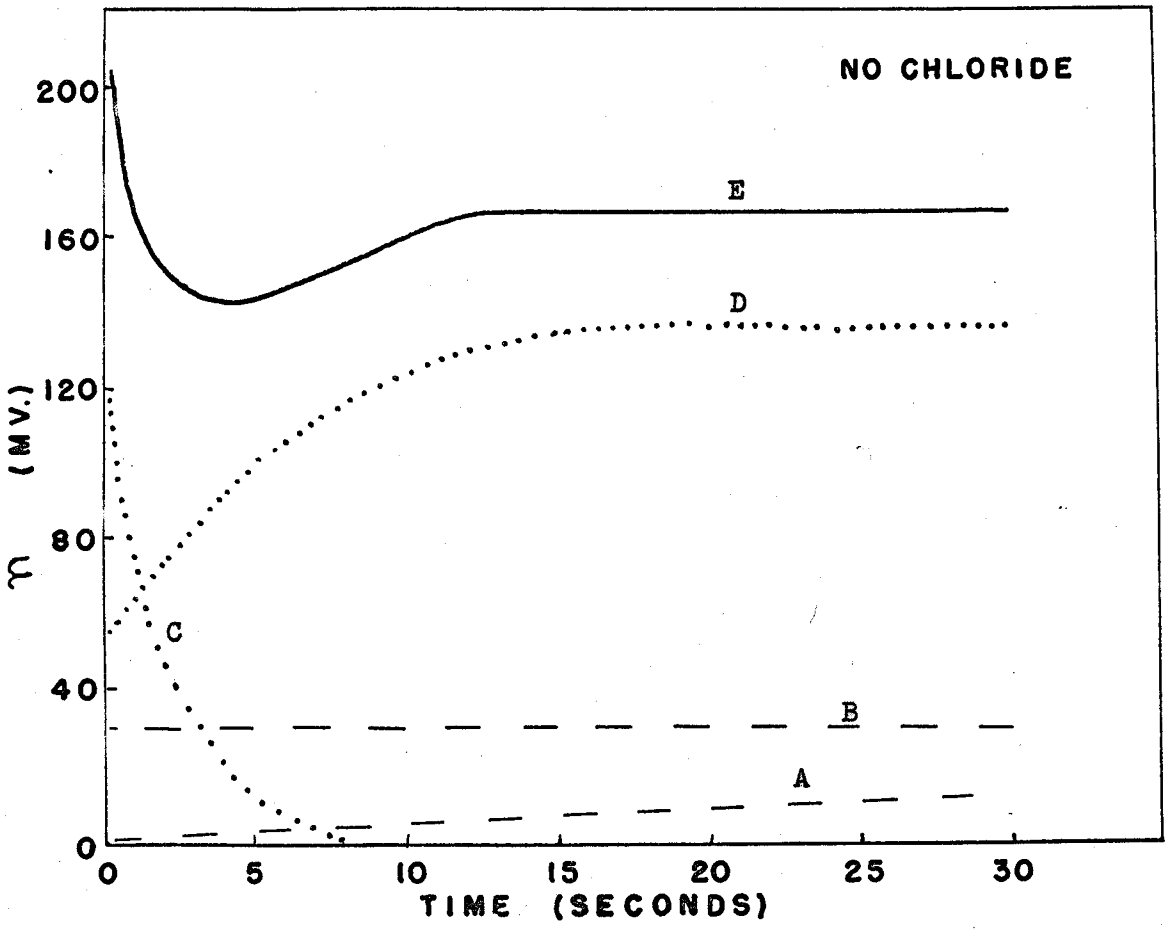


Figure 37(a) POLARIZATION CURVES; No chloride present
A. concentration B. ohmic C. reduction
D. activation E. Total

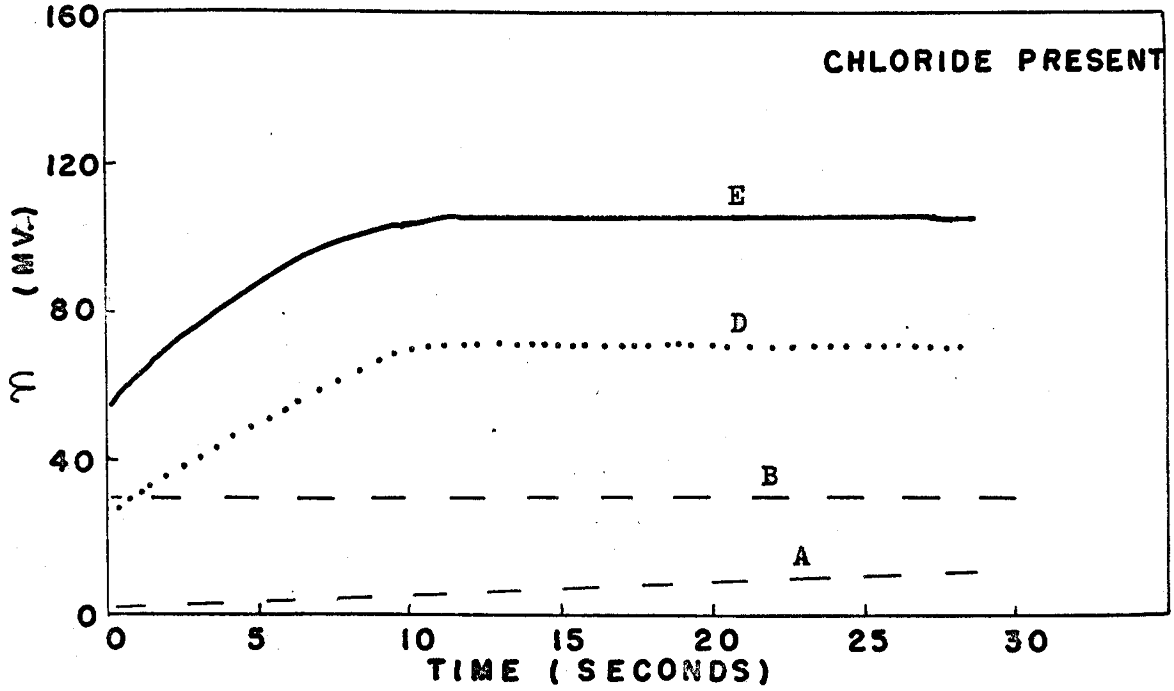


Figure 37(b) POLARIZATION CURVES; Chloride present.
A. concentration B. ohmic D. activation E. total

proximate value is known, but only the shape of the curves, these have been drawn as dotted lines so that when the total polarization (solid line) is drawn, the shape of the curve is that observed in the present work. The effect of several variables on the shape of the curves may be noted.

Temperature changes: Lowering the temperature increases the concentration of cuprous adions. As a result, as observed in Figure 32, the initial peak in the polarization curve will be less evident, and the polarization, at time intervals other than zero time, will be increased.

Changes in current density: At lower current densities the rate of increase in the polarization will be less because of the slower buildup of the cuprous adion concentration (c.f. Figures 20, 30, 31).

Increasing the halide concentration: Because the halides adsorb on the electrode before current begins to flow, the initial polarization is reduced. It has been shown that the amount of chloride adsorbed is practically constant although the concentration in the solution may change (Figure 21). As a result the initial polarization should be constant and less than that for a halide free solution. This was observed for a wide range of chloride concentrations and to a lesser extent for bromides (Figure 29).

It has been shown that the amount of chloride in the interfacial region remains essentially constant (Figure 34). As a result there will be no steady decrease with time in the polarization (e.g. Figure 29).

It has been shown that a cystine prepared surface adsorbs much more chloride than the standard surface (Figures 23 and 21). It has also been shown that the amount of chloride in the surface layer of an electrodeposit prepared from a solution containing cystine is considerably greater than that for the standard solution. It may be concluded, therefore, that the amount of chloride in the interfacial layer is increased by the presence of cystine in the solution. As a result chlorides will be stronger depolarizing agents in the presence of cystine. This was observed (c.f. Figure 28 and 29).

There are several features of the polarization curves that are not fully explained by this model. (1) The model predicts that in the presence of halides the polarization should be reduced to a value independent of the halide concentration in the solution. Instead what is observed is a steady decrease to a minimum value and then a gradual increase, (e.g. Figure 8). The minimum value occurs at a chloride concentration where a change in surface structure of the electrodeposit is visible. It also corresponds to a decrease in the amount of chloride incorporated (Figure 14). (2) It does not appear to be possible to explain the "peaks" in the curves found only at a current density of 20 ma/cm^2.

V: SUMMARY

The amount of chloride ion incorporated into a copper electrodeposit prepared from an aqueous copper sulphate solution has been determined at low chloride concentrations. It has been shown that the chloride is uniformly distributed through the depth of the deposit and that the amount is dependent on the chloride concentration in the electrolytic solution.

It has also been shown that there is a surface layer of chloride on the electrodeposit and that the amount of chloride in this surface layer is independent of the concentration in the solution within the range of concentrations used in the experiments.

The amount of chloride in the surface layer was found to be the same as that adsorbed on the surface by the proposed reaction (1).

$$CuCl^{+} + Cu_{m} \rightleftharpoons Cu_{m}Cl^{-} + Cu^{++} \qquad (1)$$

From an examination of; temperature data, current density data, and the relative enrichment upon incorporation from an electrolytic solution containing a mixture of halides, it was concluded that incorporation of halide into the electrodeposit occurs through formation of cuprous halide in the interfacial layer.

It was shown that the amount of chloride incorporated was increased when cystine was present in the solution. This was attributed to an increase in both cuprous adion and halide ion concentration in the interfacial layer.

An examination of polarization curves was made during the first thirty seconds of electrolysis. Using the above information combined with the proposal that the organic additive increases the cuprous adion concentration, it was possible to explain many of the features of the polarization curves.

GLOSSARY OF SYMBOLS

M	molarity of a solution
ma	milliamperes
Å	angstroms
G	free energy
ψ	potential between an electrode and the solution
Z	charge on an ion
e_o	electronic charge
λ	fraction of ψ acting on an ion
F^{el}	total electrostatic energy content
F	the Faraday, 96,500 coulombs mole^{-1}
N	total number of particles
i	current
i_o	exchange current
α	transfer coefficient
R	the gas constant, 8.313 joules deg^{-1} mole^{-1}
T	temperature
η	total polarization
η_A	activation polarization
η_c	concentration polarization
D	dielectric constant
V	volume
k	Boltzmann constant, 1.38 x 10^{-9} joules deg^{-1}
μ^{el}	electrostatic energy content of a particle
ψ_s	potential due to the surroundings

GLOSSARY (cont.)

Q	total charge
I	total current
R_i	resistance of resistor i
u	micro
τ	dead time
λ	lambda (= 0.001 ml.)
mv	millivolts
H	heat of adsorption
t	time
μ	activation potential
C	curie
ρ	charge density

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APPENDIX 1: CALCULATION OF THE PLATE SEPARATION OF AN IMAGINARY CAPACITOR REPRESENTING THE DOUBLE LAYER OF THE ELECTROCHEMICAL INTERFACE

Let the number of ions of either sign per unit volume in the electrolyte at an infinite distance from the metal surface be N and let $\psi_{(x)}$ be the electrostatic potential at a distance x from the interface. The number of ions of either sign at a distance x from the interface is

$$N \exp \pm (e \psi / kT) .$$

ψ as a function of x may be found by solving the well known Poisson's equation which in the present situation is one dimensional.

$$\frac{d^2\psi}{dx^2} = \frac{8 \pi Ne}{K} \quad \sinh \frac{e\psi}{kT}$$

where K is the dielectric constant for the solvent water. It will be assumed that K is independent of x, an assumption which is basically incorrect because in the high fields of the interface the water dipoles will be polarized with a consequent reduction in the dielectric constant. Only an approximate value of the plate separation is required, however, so the assumption will be adequate.

For $e\psi$ much less than kT the above equation reduces to

$$\frac{d^2\psi}{dx^2} = \frac{\psi}{x_o^2} \qquad \text{where} \qquad \frac{1}{x_o^2} = \frac{8 \pi Ne^2}{K k T}$$

and the solution is:

$$\psi = \psi_o \exp - \frac{x}{x_o}$$

where ψ_o is the potential drop between the electrode and the electrolyte at the interface.

The magnitude of the length x_o is

$$x_o \approx \frac{2.5 \times 10^{-8}}{M^{1/2}} \quad \text{cm}$$

It may be seen that for a concentration of 0.5 M, x_o is about 4 Å .

APPENDIX 2: DERIVATION OF THE TAFEL EQUATION [1]

Let the velocity of the cathodic reaction

$$M^+ + e^- \longrightarrow M$$

be $\vec{v}$ and that of the corresponding anodic reaction be $\overleftarrow{v}$. We consider the case where an electrode is functioning as a cathode; $\vec{v} \gg \overleftarrow{v}$. Let it be assumed that the velocity of the rate determining reaction is controlled by particles having more than some minimum activation potential U, and that the energy distribution is Maxwellian. It is an observed fact that as the cathode potential becomes more negative the velocity of the reaction increases. This is the result of the lowering of the activation barrier by the applied potential. The whole applied potential however may not be available to decrease the activation energy since the field extends some distance into the solution. At the beginning of the rate controlling step the reacting particles may be inside some fraction, a, of the total potential. Only the potential $(1-a)\eta$ will then be effective for the rate controlling step. The activation potential required therefore is $U - (1-a)\eta$.

The rate of the reaction may now be written as:

$$\vec{v} = K\,(C_A, C_B \ldots) \exp - \frac{U + (1-a)\eta}{RT} F$$

Except at very low current densities $i = F\vec{v}$

Therefore:

$$i = F\,K\,(C_A, C_B \ldots) \exp - \frac{U + (1-a)\eta}{RT} F$$

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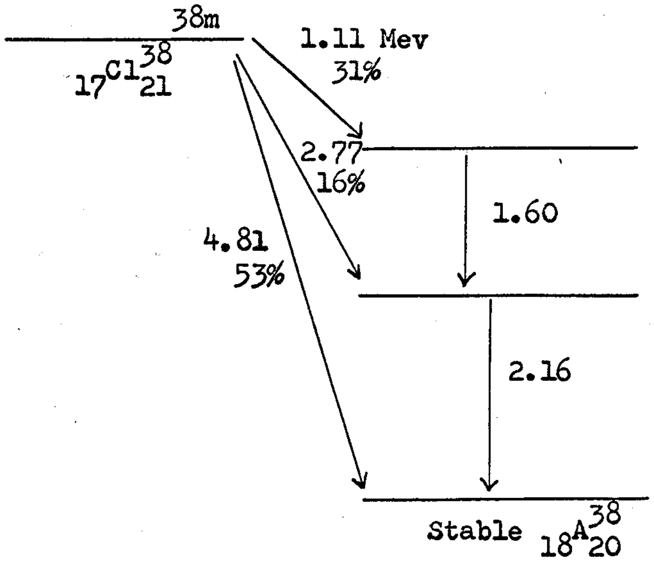
[1] This derivation follows that given by Kortüm and Bockris: Textbook of Electrochemistry, Elsevier Publishing Co., Amsterdam, 1951, p.425.

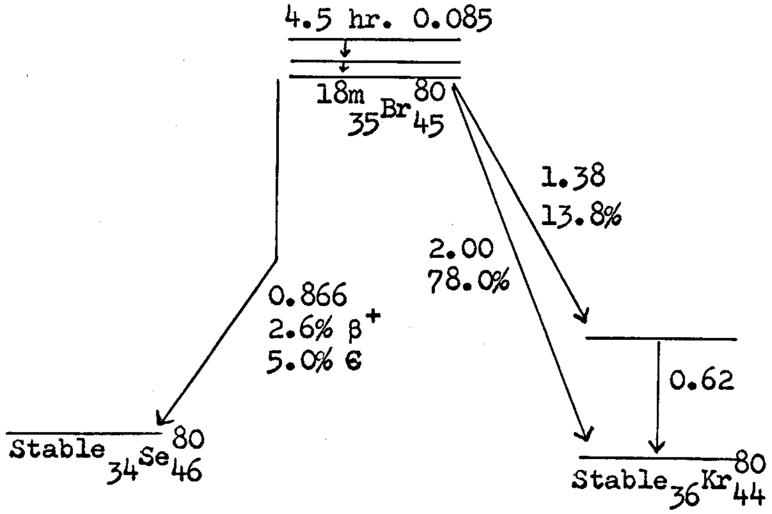
The term UF is the chemical activation energy term and η F may be written as $- Z_r e_o \Delta \psi_d$ in terms of the units used in the Introduction. In most cases $(C_A, C_B \ldots)$ may be assumed to be constant. The equation may now be written in the form used in the Introduction.

$$i = A \exp \left\{ - \left[\Delta \mu_r^{\text{chem}} - Z_r e_o \Delta \quad {}_d \alpha \right] \Big/ kT \right\}$$

where 1 - a ($= \alpha$) is the transfer coefficient.

APPENDIX 3: DECAY SCHEMES OF THE RADIOACTIVE ISOTOPES USED IN THE PRESENT WORK [1]





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[1] Nuclear Data Sheets, National Academy of Sciences - National Research Council, 2101 Constitution Ave., Washington, 25, D.C.

APPENDIX 4: CONCENTRATION POLARIZATION

The equation relating concentration polarization with time for simple diffusion at constant current is [1];

$$\eta_c = - \frac{RT}{2.30ZF} \log \left(1 - \frac{2i\sqrt{t}}{ZF\,C_o\sqrt{\pi D}} \right)$$

where $\Delta\eta_c$ is the concentration polarization

$\frac{RT}{ZF} = \frac{0.0591}{2}$ is a constant at 20° C

C_o is the concentration of Cu^{++} in the bulk (moles/ml)

Z is the charge on the ion undergoing reduction

F is the Faraday

t is the time in seconds

i is the current in amps/sec.

D is the diffusion coefficient of Cu^{++} in cm^2/sec.

Using an approximate value of 10^{-5} cm^2 sec^{-1} for the diffusion coefficient of the cupric ion the equation reduces to:

$$\Delta\eta_c = -0.03 \log (1 - 0.8\sqrt{t})$$

Values for the concentration polarization as a function of time calculated from this equation are given below:

t (sec)	η_c (mv.)
5	3
10	4
20	6
30	8
40	9
50	11
100	21
156	∞

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[1] R. C. Turner and C. A. Winkler, J. Electrochem. Soc., 99, 78 (1952).

It has been assumed that diffusion is the only mechanism bringing cupric ions to the cathode surface. This is of course unrealistic. A flat metal surface held vertically as used in these experiments has a convection current across its face. This current will increase the availability of cupric ions and will reduce the concentration polarization below the small values given in the table. It may be concluded therefore that concentration polarization is almost negligible for the times of electrolysis used in these experiments.

APPENDIX 5: CALCULATION OF CONCENTRATION OF COPPER HALIDE COMPLEXES

The concentration of the four possible copper-chloride complexes has been calculated by solving the following simultaneous equations.[1,2]

$$\frac{[CuCl^+]}{[Cu^{++}]\,[Cl^-]} = 630$$

$$\frac{[CuCl_2]}{[CuCl^+]\,[Cl^-]} = 39.8$$

$$\frac{[CuCl_3^-]}{[CuCl_2]\,[Cl^-]} = 3.09$$

$$\frac{[CuCl_4^=]}{[CuCl_3^-]\,[Cl^-]} = 5.36$$

A table of values is given on the following page.

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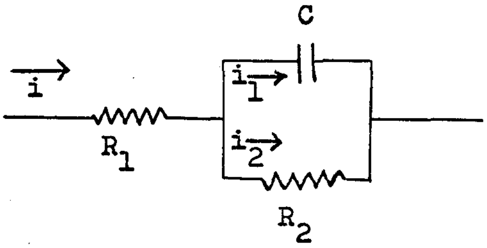
[1] Constants used in the equations are those given by H. L. Riley and H. C. Smith, J. Chem. Soc., 1448 (1934).

[2] The help of Mr. G. Norman with the computer program is gratefully acknowledged.

Cl^- added	Cu^{++}	Cl^-	$CuCl^+$	$CuCl_2$	$CuCl_3^-$	$CuCl_4^=$
			moles/liter			
1×10^{-4}	0.500	3.18×10^{-7}	1×10^{-4}	-	-	-
1×10^{-3}	0.499	3.18×10^{-6}	1×10^{-3}	-	-	-
1×10^{-2}	0.490	3.22×10^{-5}	9.95×10^{-3}	-	-	-
1×10^{-1}	0.398	3.95×10^{-4}	9.95×10^{-2}	1.56×10^{-3}	-	-
* 0.200	0.308	9.53×10^{-4}	0.185	7.02×10^{-3}	2.07×10^{-5}	1.06×10^{-7}
* 0.400	0.146	3.38×10^{-3}	0.311	4.19×10^{-2}	4.38×10^{-4}	7.94×10^{-6}
* 0.600	4.89×10^{-2}	1.03×10^{-2}	0.317	0.130	4.12×10^{-3}	2.27×10^{-4}
* 0.800	1.34×10^{-2}	2.67×10^{-2}	0.225	0.239	1.97×10^{-2}	2.81×10^{-3}
* 1.00	3.71×10^{-3}	5.64×10^{-2}	0.132	0.297	5.18×10^{-2}	1.57×10^{-2}
* 1.20	1.21×10^{-3}	9.77×10^{-2}	7.47×10^{-2}	0.290	8.77×10^{-2}	4.59×10^{-2}

* computer values

APPENDIX 6: THE TIME DEPENDENCE OF THE CHARGE ON ONE PLATE OF A CAPACITOR IN A PARALLEL RC CIRCUIT



$$i_1 + i_2 = i$$

$$i_1 = C \frac{dV_c}{dt} + V_c \frac{dC}{dt}$$

$$V_c = i_2 R_2$$

The assumption is made that $\frac{dC}{dt} = 0$. It is recognized that this is not correct but the change in the capacitance with time is expected to be small.

$$C \frac{dV_c}{dt} + \frac{V_c}{R_2} - i = 0$$

The solution is;

$$V_c = V_o e^{-t/CR_2} + iR_2$$

At time t = 0

$$V_o = V_c - iR_2$$

$$= (i_2 - i) R_2$$

$$= -i_1 R_2$$

Therefore $V_c = -i_1R_2\, e^{-t/CR_2} + iR_2$

Since $\rho = \frac{C}{A} V_c$

Then $\rho = \frac{C}{A} \left(iR_2 - i_1R_2\, e^{-t/CR_2}\right)$