Study of tin(II)/tin(IV)/anhydrous hydrochloric acid based sensitizers for electroless deposition.

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STUDY OF Sn(II)/Sn(IV)/HCl BASED
SENSITIZERS FOR ELECTROLESS DEPOSITION

by

Julio Kisel Greenblatt

A Dissertation
Submitted to the
Faculty of Graduate Studies and Research
through the Department of
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of the Requirements for the Degree
of Doctor of Philosophy at
the University of Windsor

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1988
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TO MY FAMILY

IN MEMORY OF MY FATHER
ABSTRACT

In order to enhance the reproducibility of the separate sensitization and catalyst technology Sn(II)/Sn(IV)/HCl systems were studied along three main avenues.

Kinetic studies - Data for the oxidation of Sn(II) in both concentrated and dilute HCl, Sn(IV) hydration and hydrolysis as well as reaction between Sn(II) and Sn(IV) lead to a model for the ageing of sensitizers. Linear chains of Sn(II)-Sn(IV) go on growing passing through a maximum of surface activity.

Adsorption studies - The quantitative effect of contact time with substrate, surface active agents as additives, HCl concentration, accelerators and inhibitors of Sn(II) oxidation as well as ageing effects on these factors are included to support the model.

Transmission electron microscopy - Correlation between the adsorption of sensitizers and the metal deposits they produce indicate that the higher the amount adsorbed, the smaller average metal islands. The nucleation density increases with adsorption exponentially. Crystallite size distributions are narrow and not affected by sensitization. Overgrown colloids in the sensitizer lead to scattered clusters of islands. Maximum adsorption corresponds to a bimodal island size distribution: very small islands and large ones that reflect the initiation of the colloidal aggregation.
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Apparatus Used for Casting Films
Film Flotation
Grid Mounting
Human Brain Image Processing
Image Digitalizing Instrumentation
CHAPTER I
TECHNICAL BACKGROUND

At the present time, metals can be deposited onto nonconductors using one of the following techniques.

- A variety of methods which make use of a vacuum bell. Metal is evaporated using a number of techniques, (e.g. RF, electric current etc.). The metal atoms then travel in a rectilinear path and are deposited on any unmasked spot inside the bell. There are different ways used to modify this path. One is by an outside force field onto a desired target. Such techniques produce the best planar films in terms of uniformity and purity; however they are very expensive due to the vacuum system required.

- A process similar to painting. Reduced suspended metal is brushed or sprayed onto a substrate.

- Attaching metal foil by ironing it or gluing it to the substrate.

- Pyrolitic reduction. Used only when the substrate can withstand high temperature. Metal salt is deposited on the substrate, usually by drying a solution and then reducing the metal by thermal action.

- Homogeneous chemical reduction. There are two main variations: i) A reducing agent is brought in contact with a substrate that has metal salt on the surface. ii) Two jets, one containing the solution with the metal salt to
be reduced, and the other containing the reducing agent, are made to collide on the surface of the substrate; the metal is reduced and attached in situ.

Electroless deposition. The main method used at present to coat metal in the liquid state onto nonconductors.

The name "electroless deposition" is somewhat misleading, because although there are no external electrodes, there is electrical current involved. Instead of an anode, the metal is "supplied" by the metal salt; replenishment is achieved by either adding salt or by an external loop with an anode that has higher efficiency than the cathode. There is, therefore, instead of a cathode to reduce the metal, a substrate serving as cathode, while the electrons are provided by a reducing agent.

Electroless deposition is autocatalytic, and it is initiated by active metals upon immersion in an electroless bath.

Because each substrate requires its own specific technique, depositing active metal onto the surface of a nonconductor is an art. In general, deposition requires one or more of the following steps: cleaning, surface modification (roughening, etching, etc.), sensitization and subsequent catalyzing or catalyzing and activating. Additional rinsing is also required between steps. Figure I-1 illustrates the processes.
Figure 1-1. Electroless Deposition Process
"Sensitization and catalyzing" mean, in this context, adsorbing molecules from a solution such as acidic Sn(II) and/or Sn(IV). Other much less frequently used sensitizing agents are AgNO₃, AuCl₃, metallic Na (in naphthalene solution) etc. An oversimplified model assumes that the sensitizing ion can reduce the active metal from the catalyst solution, usually PdCl₂. (Au, Pt, Rh, Os and Ag solutions have also been used) eg:

Sn²⁺ + Pd²⁺ → Sn⁺⁺ + Pd⁰

If the metal to be deposited electrolessly can be reduced by the sensitizing ion, then it is not necessary to reduce the active metal first. Instead, the substrate is immersed in the electroless bath immediately after sensitizing and rinsing (e.g., electroless Cu or Ag when using Sn(II) based sensitization).

The alternate method, "catalyzing and activating", makes use of a "mixed colloidal catalyst" bath. The colloid is reduced Pd, stabilized by "Sn(II) and Sn(IV) ions". The activation step is the removal of the layer formed by the stabilizing agents with KF-HF or other chemicals, such as HCl, NaOH etc. In some cases, the activation step can be omitted, but the plating solution gets contaminated. There are many proprietary and patented processes reported. One, verified by us, is by D'ottavio [1].

During the last decade, the mixed colloidal technology has captured most of the market. The reasons given for this
wide usage are that it comprises one step only, and so is more economical. Actually, it also requires two steps, since the activator requires a separate bath. It is, however, more reproducible than the separate Sn-Pd technology, and that is the reason for it being considered more economical. The following observations compare the two technologies:

- An object emerging from the mixed colloidal bath is covered by a Pd layer which can be inspected visually. No visual inspection is possible during the Sn-Pd process.
- Mixed colloidal solutions are very stable and do not exhibit noticeable ageing effects. The Sn solutions do present ageing effects; they perform for a short period of time after first being aged for some initial period. These lengths of time are arrived at through trial and error, without a clear understanding of the chemistry involved.
- Mixed colloidal solutions are very resistant to impurities; Sn-based solutions are very sensitive to impurities.
- Surface preparation is not as critical in the mixed colloidal case as it is with Sn based solutions.

It has been recognized in the latter case that besides being clean, surfaces must be hydrophilic in order to be wetted by the sensitizing solutions. There are claims that the bonding takes place because of mechanical entrapment and hindrance, and therefore a rough surface is required [2][3]. On the other hand, there are many examples in the literature
of successful sensitization of very smooth surfaces, such as glass slides, for instance. This indicates that besides mechanical bonding there are other adhesion mechanisms, which under certain circumstances become dominant.

The importance of surface functional groups has been recognized by few researchers [4]. Ehrbar et al. [5] used corona discharge to deglaze different polymers. They also compared, by using several polymers, the nature of electroless deposits and adhesion on deglazed versus non-deglazed surfaces. In general, corona-discharged surfaces have better coverage and adhesion, though not always. For example, measured by the adherence characteristics of the final deposit, polyesters from different manufacturers respond differently to the deglazing treatment. All in all, there is no readily apparent reason based on bulk chemical composition, why some polymers have good metallization and adherence while others do not.

Another proof of the role of surface-functional groups is the fact that industry has spent many years unsuccessfully trying to metallize completely covalent substrates, such as silicon wafers [6].

Despite the previously mentioned disadvantages of using the Sn-Pd process, sometimes the initial nucleation density that is achieved using this technology is an order of magnitude greater than what can be achieved using the mixed
colloidal technology. Hence a continuous film can be obtained at smaller thicknesses. Such an achievement translates into:

- Economical advantage, since less metal is needed when the only purpose is to render the material conductive.
- Better adhesion due to higher density of fastening sites.
- Potential for the development of special products where very thin coatings are needed.

In order to better understand the technology of electroless deposition onto nonconductors, a summary of the history of the process follows.

Some reactions that are known since the previous century, such as those which involve the Tollens and Fehling reagents, are chemical reductions on which some of the electroless baths used today are based. There is evidence that the mirror industry knew about electroless deposition of Ag on flat glass cast on molten Sn [7], but the technology was kept secret. The process itself as a metal deposition technique was invented in 1944 by Abner Brenner [8], who gave it the name "electroless deposition".

Although Brenner developed the Sn-Pd technology in order to metallize plastics, the main interest at that time was electroless Ni deposition onto metals. With objects of complex geometry, electroplating presents problems associated with current density distribution; Electroless deposition does not, and the Ni-P metallic glass obtained has some very desirable properties (e.g., corrosion resistance to certain
environments, hardness after heat treatment). Indeed, Brenner rediscovered the fact that NaH₂PO₂·H₂O can reduce Ni²⁺ to its metallic state. He did this by electroplating Ni-P alloys and noticing that the cathode efficiency was greater than 100%. This indicated that Ni²⁺ was not only being reduced by the external electric current.

The interest in electroless deposition onto plastics was awakened in the mid fifties both in connection with printed circuit board industry and in the field of decorative plating.

The first attempts at systematic research were made by platers, hence electroless deposition onto nonconductors evolved in an empirical fashion. Later, metallurgists and physicists studied the process, but concentrated mostly on specific aspects: post-treatments of the metal deposited [9], the structure of the deposit obtained when using different baths [10][11], the electroless bath itself with respect to the rate of deposition under different conditions [12][13]. It was not until the late sixties and early seventies that attention was focused on the sensitizing systems [14]. Even then, the sensitizer solutions were not studied but rather the sensitized surfaces. By this time, some technological facts about the ageing of the Sn(II) based sensitizers were known, and were attributed to the oxidation of Sn(II) to Sn(IV).

Meanwhile, models and observations that rendered previous models obsolete began to accumulate in the literature, for example:
- Sn(II) has to be present in the sensitizer, since after being adsorbed its redox reaction with Pd(II) leaves the active metal on the surface.

- Metallization was obtained using aged Sn(IV) without any Sn(II) being added [15].

- Sn(II) solutions are more effective as sensitizers when aged for a certain period of time than when they are freshly prepared solutions [16]. Fresh mixtures of Sn(II) and Sn(IV) are not as effective as aged Sn(II) or fresh Sn(II) plus aged Sn(IV) mixtures [17].

- By irradiating a masked substrate with U.V., positive or negative metallized images can be obtained depending on where in the process irradiation take place, and the pH of the electroless bath [18].

Although fundamental research on solutions prepared with SnCl₂·2H₂O and dilute HCl was an active field in the past, owing to shifting of the interests of inorganic chemists this field has been inactive during the past thirty years.

The objective of our research is to obtain a better fundamental understanding of the ageing of Sn-based sensitizers in aqueous HCl solution. Such an understanding should render the sensitization process more reproducible.
CHAPTER II
LITERATURE REVIEW

The first systematic research on the oxidation of Sn(II) chloride was reported by Young [19] in 1900. His experimental approach was to shake a solution of Sn(II) in an atmosphere of pure O₂ and then to measure the decrease in volume at atmospheric pressure inside a thermostated bath. This was done by means of a gas burette. Young made the following observations:

- At high rate of agitation, the rate of O₂ consumption does not increase, so the process is not mass transfer limited.
- Rate of oxidation of the solution increases with time. A product of the reaction system, either of Sn(II) oxidation or from a side reaction, acts as an accelerator.
- Reaction rate increases with HCl concentration.
- Reaction is extremely sensitive to minute amounts of pollutants. The following materials act as accelerators: rubber, Fe, Cu, H₂S, ethanol. There are also deaccelerators: Mn, Cr, tobacco (and tobacco smoke), brucine, morphine, aniline, KCN etc..
- A mechanism for the reaction is proposed (product first formed is Sn(IV) chloride, which then slowly hydrolyses):

\[
\text{SnCl}_2 + 2\text{HCl} + \frac{1}{2}\text{O}_2 \rightarrow \text{SnCl}_4 + \text{H}_2\text{O}
\]
SnCl$_4$ + 4H$_2$O ----> Sn(OH)$_4$ + 4HCl

The equation for the overall reaction:
SnCl$_2$ + 3H$_2$O + 1/2O$_2$ ----> Sn(OH)$_4$ + 2HCl

• Time between preparation of the solutions and beginning of O$_2$ admittance was varied in order to evaluate the possible effect of hydrolysis of the Sn(II) ion. The effect of HCl concentration on the possibility of hydrolysis was also studied; these results were inconclusive.

• When Sn(II) chloride is oxidized by free Cl$_2$ or when Sn(IV) chloride is mixed with Sn(II) chloride, the solution turns yellow. Young's solutions showed that colour. The yellow colouration was deeper in solutions with less HCl. Young interpreted this to mean that the formation of Sn(IV) is bypassed by the hydrolysis reaction, and that the first effect of the increase in HCl concentration is to drive back hydrolysis if the solution has already been hydrolyzed.

Two aspects which are not dealt with in Young's experiments are:

• Consideration of changes in O$_2$ solubility with changes in liquid composition.

• Consideration of other reactions that may be taking place simultaneously.

During the early thirties, Walton and co-workers published a series of articles about the oxidation of Sn(II) [20][21][22]. The experimental set up described was similar to
the one previously used by Young. Their findings can be summarized as follows:

- Amount of $O_2$ consumed is that which is theoretically required for complete oxidation of Sn(II).
- Uniform and reproducible results are not obtained until approximately 10% Sn(II) has been oxidized.
- Paraffin and glass have no effect on the reaction rate.
- At a strength below 0.25M HCl, reaction rate is independent of HCl concentration, but it is proportional to it at higher concentrations.
- Effect of temperature was studied, but the results are neither consistent nor reproducible, since the order of reaction seems to vary with temperature.
- Visible light has no effect on reaction rate, but U.V. light below 307 nm is absorbed totally and it speeds up the reaction considerably.
- Partially oxidized Sn(II) solutions gave positive indication of peroxide when tested with Ti(SO$_4$)$_2$. No peroxide showed after full oxidation, leading to the conclusion that the peroxide must be an intermediate. (This peroxide has never been isolated).
- Since the quantum yield of the photochemical oxidation was greater than one, the oxidation is assumed to be a chain reaction.
- Accelerators and inhibitors show the same effect on photochemical as on thermal reactions, leading to the
conclusion that the reaction without U.V. is also a chain reaction.

- From Beer's law: The molecular absorption coefficient is not a constant, but a function of Sn(II) and HCl concentrations.

- The absorbing medium must be some substance whose concentration increases with addition of HCl, hence one of the following: HSnCl₃, H₂SnCl₄, SnCl₂⁻ or SnCl₄²⁻.

- Correlation between the activity and structure of many promoters and inhibitors of the oxidation reaction was attempted, but without success.

In 1953, Baker [23] confirmed the chain reaction mechanism, studied inhibition as a function of the concentration of the inhibitor, and distinguished two cases: where the inhibitor is consumed and where it is not.

The first recognition of a reaction between Sn(II) and Sn(IV) in HCl solutions was in 1951 in two papers by Craig et al. [24][25]. They used spectrometric and radiochemical techniques, and postulated that the non-additive light absorption of Sn(II) + Sn(IV) solutions is due to a dimeric complex containing one Sn(II) and one Sn(IV) ion.

Craig also stated that the limiting step is an electron exchange reaction, and that the interaction dimer is "unsymmetrical", but no details were provided to support these conclusions.
Craig also discarded the possibility of a monomeric complex of Sn(III). This is important, since the possibility of Sn acting with valence III had been postulated in connection with other oxidation reactions of Sn(II) e.g. oxidation of Sn(II) by Ce (IV) [26]. At the present, however, cases of Sn acting with valence III are well documented [27]. In all the known cases it is used as a means to explain reaction mechanisms in organic synthesis [28][29].

The concentrations of both Sn salts and HCl in Craig's study were much higher than in a typical sensitizer.

The early fifties were the most active period for fundamental research on Sn(II) and Sn(IV) solutions; nevertheless, there were no new findings. The reactions previously described were studied in other media [30][31], such as HClO₄, H₂SO₄, ethanol. Although mechanisms were proposed and kinetic data was given, no useful information could be deduced which would be applicable to aqueous HCl media.

In 1966, Paul et al. [32], using very dilute solutions, obtained the stoichiometry of the complex $[\text{Sn(II) / Sn(IV)}] = 1/4$.

At first glance, it is tempting to believe that the results may have been due to a different behaviour of Sn(II) and Sn(IV) solutions in the very dilute regime. (Current results however, do not suggest this to be the case).
The only other publication on this subject in the last two decades or more was by Beltran and Borras [33]. Their findings may be summarized as follows:

- The stoichiometry of the yellow complex is $[\text{Sn(II)} / \text{Sn(IV)}] = 1$.
- The reaction between Sn(II) and Sn(IV) is not direct but requires hydrolysis products from both Sn(II) and Sn(IV).
- Hydrolysis of either Sn(II) or Sn(IV) is very slow.
- At equilibrium Sn(II) is only slightly hydrolyzed in 0.24M HCl.

So far, this literature review has chronologically covered the subject of oxidation of Sn(II) to Sn(IV), and the formation of an Sn(II)-Sn(IV) based product. A parallel development occurred which concentrated on the complexation and hydrolysis reactions of Sn(II) and Sn(IV) chlorides in aqueous HCl media.

During the past century, researchers concluded that formation of complexes between Sn(II) and Cl⁻ occurs. This was so, since the solubility of SnCl₂ increases tremendously with augmenting HCl concentrations.

Young [34] noticed that: i) The conductivity of a Sn(II) chloride solution in 0.2M HCl increased with time. ii) increasing the HCl concentration to 0.5M resulted in steady conductivity. It was concluded that the effect was due to the hydrolysis of Sn(II), and not because of its oxidation.
Young's measurements indicate a "large" hydrolysis constant and a "slow" reaction rate. No quantitative values are given.

Young also studied the effect of KCl and KI instead of HCl in Sn(II) chloride solutions. Since no existing theory of mixed electrolytes could explain the behaviour of these systems, the following conclusions were drawn:

- SnCl₂ forms with HCl two distinct association complexes, one is considerably more sensitive to dilution than the other.
- KCl shows a greater power of association at high concentrations than HCl does. KI shows a still higher power of association.

Garret and Heiks [35] studied the solubility of SnO in dilute solutions of HCl, and evaluated the following data for SnO:

- Initial acidic dissociation.
- Solubility product constant.
- Free energy of formation.
- Enthalpy of formation.
- Heat of hydration.

Although Garret's system is at first glance completely different from a typical Sn(II) based sensitizer system, the two share some common equilibria. Garret's paper also presents a compilation of equilibrium and thermodynamic data for Sn oxides and hydroxides that summarizes the state of
knowledge up to roughly 1940 (the article was published in 1941).

Although the stability constants of Sn(II) chloride solutions were extensively studied during the forties, there were disparities among the researchers with respect to both the number of equilibrium constants and their actual values. An experimental procedure was described in 1951 by Vanderzee and Rhodes [36]. They considered the combined effect of hydrolysis and complexation of the Sn(II) ion. They used the following simple model:

In solution containing Sn²⁺ and Cl⁻ ions, the equilibria are:

\[ \text{Sn}^{2+} + n\text{Cl}^- \rightarrow \text{SnCl}_{n}^{2-n} \quad n = 0, 1, 2, \ldots, m \]

\[ K_n = \frac{[\text{SnCl}_{n}^{2-n}]}{[\text{Sn}^{2+}][\text{Cl}^-]^n} \]

If the Sn(II) ion undergoes hydrolysis, there is one more equilibrium:

\[ \text{Sn}^{2+} + \text{H}_2\text{O} \rightleftharpoons \text{SnOH}^+ + \text{H}^+ \]

\[ h = \frac{[\text{SnOH}^+][\text{H}^+]}{[\text{Sn}^{2+}]} \]

\[ \text{SnOH}^+ + n\text{Cl}^- \rightarrow \text{Sn(OH)}\text{Cl}_{n}^{1-n} \]

This model considers the existence of mixed complexes of the following form: Sn(OH)Clₐ⁻ⁿ. With the corresponding equilibrium constants:
\[
\delta_n = \frac{[\text{Sn(OH)Cl}^{1-n}]}{[\text{SnOH}^+]^n [\text{Cl}^-]^n}
\]

The experimental method used by Vanderzee et al. involved EMF measurements using a concentration cell at a constant ionic strength of 3.0.

The data analysis allowed them to determine the equilibrium constants \( K_n \), the hydrolysis constant \( h \), the first mixed equilibrium constant \( \delta_1 \), and to infer that if \( \delta_2 \) and \( \delta_3 \) exist, they must be much smaller than \( K_2 \) and \( K_3 \) respectively. The results of Vanderzee's experiments are summarized in Table II-1.

**TABLE II-1**

<table>
<thead>
<tr>
<th>Summary Of Vanderzee's Equilibrium Constants</th>
</tr>
</thead>
<tbody>
<tr>
<td>Constant</td>
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<tr>
<td></td>
</tr>
<tr>
<td>----------</td>
</tr>
<tr>
<td>( h )</td>
</tr>
<tr>
<td>( \delta_1 )</td>
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<tr>
<td>( K_1 )</td>
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<tr>
<td>( K_2 )</td>
</tr>
<tr>
<td>( K_3 )</td>
</tr>
</tbody>
</table>

It can be noted that three constants \( K_n \) describe the data instead of four, as would be expected from the knowledge of valence theories. Schaap et al. [37] studied an analogous system, complexes of Sn(II) in F- solutions. They also found
the existence of a coordination number of three between Sn(II) and F⁻.

Gorman [38] studied the hydrolysis of Sn(II) in HClO₄ solutions, the results of this research estimate that at equilibrium, at most 2% of the total Sn(II) is hydrolyzed. According to Ries [39], when O₂ is completely excluded, acidic Sn(II)-based sensitizers do not present an ageing effects. Morgan [40] claims this same result, and states that Sn(II) does not hydrolyze, and that the hydrolysis identified is due to careless exclusion of O₂, with the ultimate production of hydrolysis products of Sn(IV).

Pourbaix [41] compiled data and made potential–pH equilibrium diagrams for Sn (also for Cl among others). Although many compounds of potential interest were identified, the diagrams have the following limitations:

- The diagrams are for equilibrium, while Sn-based sensitizers work only in nonequilibrium conditions. When they reach equilibrium they are rendered useless.
- The region of the diagrams corresponding to sensitizers, Pourbaix recognized these as not completely characterized.
- There are no clear rules about how to mix the Sn and the Cl diagrams.

Linganae [42][43] developed the polarographic determination of Sn(IV) in 4M NH₄Cl + 1M HCl; some conclusions from his work are:
At low to moderate [Cl⁻] (approximately [Cl⁻] < 1M), the Sn(IV) ion is hydrated quantitatively.

At high [Cl⁻], virtually all Sn(IV) is transformed to SnCl₂⁻.

The formation of SnCl₂⁻ is the basis for preserving stock solutions of Sn(IV) in concentrated HCl, and of the polarographic analysis of Sn(IV) in 4M NH₄Cl + 1M HCl.

To conclude this section, it is safe to state that very little of the quantitative analytical chemistry and kinetic data about Sn-based sensitizers is accurate. Because all researchers are limited by the existent technology at the time.
CHAPTER III
EQUILIBRIUM AND KINETIC STUDIES

Considering the reactions that most likely take place in a typical sensitizer, experiments were devised to determine whether these reactions do actually take place, and if they do, at what rate. Combining these reactions, a model is provided which can explain qualitatively the ageing of Sn-based sensitizer solutions.

Whenever conditions for the study of each reaction were chosen, attempts were made to insulate them as much as possible from other reactions that might occur either in series or in parallel.

The study was divided into four sections, according to the four most significant processes involved.

A. Complexation of Sn(II) and Cl- Ions

To determine the Sn(II)-Cl- complexation constants, the method developed by De Ford and Hume [44] was used. This method makes a number of assumptions:

- The reduction product forms an amalgam, or diffuses into the Hg drop.
- The concentration of the complex-forming agent (Cl-) is large enough that its concentration at the Hg drop surface equals its bulk concentration.
The diffusion coefficient of all the complexes and the free cation have the same value. An extension of the method, for the case where the diffusion coefficients of the complexes and the free ion differ considerably, was given by Kacena and Matosek [45]. In the present system as well as in most systems involving simple anions, no correction is necessary. The diffusion coefficients of the species in the system are very similar. An explanation [46] in the case of the first and second complexes is that the increase in bulkiness due to the addition in Cl⁻ ions is compensated by the decrease in size of the hydration sphere.

With the previous conditions in mind, the following equation applies:

\[
(E_{1/2})_{\text{complex}} - (E_{1/2})_{\text{free}} = \frac{-RT}{nF} \ln \sum_j K_j [X]^j
\]

(1)

\(X\) being the anion Cl⁻.

New variables are defined:

\[
\delta E_{1/2} = (E_{1/2})_{\text{complex}} - (E_{1/2})_{\text{free}}
\]

(2)

\[
F_0(X) = \sum_j K_j [X]^j = \exp \left( \frac{-nF}{RT} \delta E_{1/2} \right)
\]

(3)

On a \(F_0(X)\) vs. \([X]\) graph, the intercept on the \(F_0(X)\) axis when \([X]\) \(\rightarrow 0\), gives the value of \(K_0\), since:

\[
F_0 = K_0[X]^0 + K_1[X]^1 + K_2[X]^2 + \ldots + K_m[X]^m
\]

(4)

\[
\lim_{X \rightarrow 0} F_0 = K_0 = 1.0
\]

(5)

\(X \rightarrow 0\)
Note that $K_0$ has to be equal to one. This can be used to check the accuracy of the experimental results.

By the same procedure, it follows that defining:

$$F_j(X) = \frac{F_{j-1} - K_{j-1}}{[X]}$$  \hspace{1cm} (6)

From $F_j(X)$ vs. $[X]$ graphs, the intercept on the $F_j(X)$ axis extrapolating for $[X] \rightarrow 0$ gives the value of $K_j$.

For a complex $\text{SnCl}_{2-}$ not to exist, $K_r = 0$ which implies that $F_r = 0$, therefore:

$$F_{r-1} = K_{r-1} = \text{constant}$$  \hspace{1cm} (7)

Hence, a plot of $F_{r-1}$ vs. $[X]$ has to be a straight line parallel to the $[X]$ axis. Carrying this analysis further:

$$F_{r-1} = \frac{F_{r-2} - K_{r-2}}{[X]}$$  \hspace{1cm} (8)

$$F_{r-2} = F_{r-1}[X] + K_{r-2} = K_{r-1}[X] + K_{r-2}$$  \hspace{1cm} (9)

$$F_{r-3} = \frac{F_{r-2} - K_{r-3}}{[X]}$$  \hspace{1cm} (10)

So for $n$ complexes:

$$F_0(X) = K_n[X]^n + K_{n-1}[X]^{n-1} + \ldots + K_1[X] + 1$$  \hspace{1cm} (11)

In order to apply this method, $E_{1/2}$ for the reduction of the free ion at different ionic strengths must be known. For this purpose, the values for the reduction of $\text{Sn(II)}$ in $\text{ClO}_4^{-}$ solutions as reported by Schapp et al. [47] were used. The range of ionic strengths that we covered was slightly wider.
than the one reported; extrapolation was used to calculate the extremities.

Distilled H₂O was boiled and cooled under bubbling zero grade N₂. Unless specified otherwise, this H₂O was used exclusively for the experiments described in this chapter. It will later be referred to as "oxygen free water".

A solution 1.0E-03M SnCl₂·2H₂O + 0.1M HCl was transferred into a polarographic cell. The various Cl⁻ concentrations were attained by making additions of necessary amounts of a 4M NH₄Cl solution. Then the polarograms were obtained.

For the polarograms, the range of ionic strengths covered was from 0.4 to 3.0. The measurements were carried between 25 and 50°C in intervals of 5°C.

Figure III-1 shows the F₁ vs. [X] curves at 25°C. Only three equilibrium constants were obtained. In the literature review emphasis was placed on Vanderzee and Rhodes results because they also obtained only three equilibrium constants. This is, however, the only similarity between their results and this study, since the values involved are entirely different.

Knowing from the data analysis at 25°C that three constants describe the system, the F₀ functions at the other temperatures were obtained by parameter fitting using cubic polynomials.

Although least squares fitting of polynomials is a well established subject, we consider worth mentioning that the
Figure III–1. $F_j$ vs $[X]$ at 25°C
software of Carnahan et al. [48], McCalla [49] do not perform adequately. When the \( F_0 \) were fitted with them some coefficients were negative and \( K_0 \) was far from 1.0 (physically impossible). Furthermore, the coefficients were highly sensitive to changes in the precision of the computations (there were even changes in sign!). When tested with known polynomials, these source codes perform well for straight lines, poorly for square polynomials and do not perform at all for cubic ones. In searching for the cause of this behaviour, Forsythe et al. [50] report similar difficulties to those we have found, and made an in depth analysis of the problem, which arises because the normal equations lead to very "badly behaved" matrices, unsuitable to be solved by variations of Gaussian elimination. Forsythe et al. [51] solve the problem using singular value decomposition of the matrix. The subroutine was written by Golub and Reinsch [52] and the source code is listed in Forsythe's book. When this software was used, the polynomial coefficients were weakly dependent on the precision of the computations, all the coefficients were positive and \( K_0 \)'s were in the vicinity of 1.0.

The coefficients of the \( F_0 \) polynomial are the different equilibrium constants as was shown previously. Table III-1 summarizes the values obtained for the equilibrium constants. Appendix C compiles graphically the equilibria of the Sn(II) species obtained using the equilibrium constants, for the range \( 0.05 \text{M} < [\text{Cl}^-] < 1 \text{M} \).
TABLE III-1

Equilibrium Constants

<table>
<thead>
<tr>
<th>Temperature °C</th>
<th>$K_0^*$</th>
<th>$K_1$</th>
<th>$K_2$</th>
<th>$K_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>1.09</td>
<td>9.78</td>
<td>36.4</td>
<td>67.25</td>
</tr>
<tr>
<td>30</td>
<td>0.98</td>
<td>14.25</td>
<td>44.2</td>
<td>69.47</td>
</tr>
<tr>
<td>35</td>
<td>1.11</td>
<td>17.3</td>
<td>57.6</td>
<td>72.14</td>
</tr>
<tr>
<td>40</td>
<td>1.05</td>
<td>19.8</td>
<td>69.8</td>
<td>77.8</td>
</tr>
<tr>
<td>45</td>
<td>1.01</td>
<td>22.1</td>
<td>83.4</td>
<td>83.7</td>
</tr>
<tr>
<td>50</td>
<td>0.89</td>
<td>23.6</td>
<td>99.1</td>
<td>88.5</td>
</tr>
</tbody>
</table>

# Theoretically $K_0 = 1.0$

The polynomial fit for the different temperatures is shown in Figure III-2.

A set of measurements was performed for the Sn(II) containing solutions, which were aged for one week under $N_2$ atmosphere at 30°C. The results were practically the same as those for unaged solution, thus verifying the assumption that hydrolysis of Sn(II) does not play any significant role in the system.

B. Oxidation of Sn(II) to Sn(IV)

From background information, it is known that mechanistically there are at least two reaction paths, one of
Figure III-2. Cubic Polynomial Fit For $F_0$
which is dominant at \([H^+] > 0.25M\), and the other at \([H^+] < 0.25M\), which involves a chain reaction.

A non-elementary representation of the oxidation reaction at high \([H^+]\) can intuitively be written:

\[
\text{Sn}^{2+} + 2H^+ + 1/2\text{O}_2 \rightarrow \text{Sn}^{4+} + H_2O
\]

This reaction is the one responsible for the oxidation of stock solutions of Sn(II) in concentrated HCl.

A typical stock solution consisting of \(100 \text{ g SnCl}_2\cdot2\text{H}_2\text{O} + 36.5\% \text{ HCl}\) to make up \(200 \text{ mL}\) was studied by analyzing it polarographically for Sn(IV) after different time periods. The study was at room temperature (approximately \(23^\circ\text{C}\)).

There were no provisions made to exclude \(\text{O}_2\) from this system for the following three reasons:

- This conforms to normal practice.
- The amount of oxygen absorbed in concentrated HCl solution is expected to be fairly small, much below the saturation limit in pure \(\text{H}_2\text{O}\).
- To produce concentrated HCl in oxygen free water, HCl has to be displaced from aqueous solution (by addition of \(\text{H}_2\text{SO}_4\) or other strong dehydrating agents to concentrated aqueous HCl). The expelled HCl vapours then have to be absorbed into oxygen free water. With the limited physical facilities available, this is a dangerous practice.

*Other oxidation reactions have been considered, in which the oxidizing agent is either "free" water or hydration water.*
The data obtained is shown in Table III-2. These data failed to fit any elementary kinetics, probably because the reaction was controlled by $O_2$ diffusion. This variable was not controlled; the solution was initially prepared in a volumetric flask, and then transferred to a bottle which was opened only during sample retrieval.

**TABLE III-2**

Oxidation of Sn(II) From Stock Solutions

<table>
<thead>
<tr>
<th>Time (minutes)</th>
<th>[Sn(II)] molar</th>
<th>Time (minutes)</th>
<th>[Sn(II)] molar</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>2.22</td>
<td>70</td>
<td>0.69</td>
</tr>
<tr>
<td>10</td>
<td>2.10</td>
<td>80</td>
<td>0.44</td>
</tr>
<tr>
<td>20</td>
<td>1.96</td>
<td>90</td>
<td>0.25</td>
</tr>
<tr>
<td>30</td>
<td>1.71</td>
<td>100</td>
<td>0.11</td>
</tr>
<tr>
<td>40</td>
<td>1.48</td>
<td>110</td>
<td>0.03</td>
</tr>
<tr>
<td>50</td>
<td>1.22</td>
<td>120</td>
<td>----</td>
</tr>
<tr>
<td>60</td>
<td>0.96</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Two points should be noted:

- The oxidation in this medium proceeds very fast.
- The solution turns yellowish at the end of the reaction, indicating the likely presence of the Sn(II)-Sn(IV) adduct, but no Sn(II) is detected polarographically, indicating that the presumed adduct unit remains associated; thus it is different from the identified
Sn(II)–Sn(IV) unit formed in less concentrated HCl solutions.

A report [53] of sensitization by Sn(II) using stock solutions of the same composition as the one studied here was located, but most likely had very little if any free Sn(II) left.

The experimental procedure for studying the oxidation at low [H+] is as follows:

Solutions of varying amounts of SnCl₂·2H₂O and HCl were made using oxygen free water under bubbling N₂. These solutions were transferred to glass bottles. Three holes were drilled in each of the bottle caps. A small circle of soft rubber was supported on a large circle of hard rubber and placed against the inside of each cap as shown in Figure III–3. The bottles were sealed with the caps on, using silicon rubber. Next, they were placed inside a bath of constant temperature. After a period long enough to achieve thermal equilibrium, the solutions were further degassed with zero grade N₂ for a small period of time. This insured complete degassing without causing a considerable amount of HCl to be lost. Controlled amounts of O₂ were injected using H₂O₂ 30% solution (Sn(II) catalyzes the decomposition of H₂O₂). Immediately after the injection, all the needles were removed and a drop of toluene was placed on top of the holes. This was done because the soft rubber swells and therefore the bottles remain pressurized.
Figure III—3  Sample Preparation Under Nitrogen Atmosphere
After a short time, in the tests this ranged from 15 minutes at 30°C to 5 minutes at 50°C, a sample was retrieved by using a syringe and was immediately analyzed polarographically. In this way, the amount of Sn(IV) present was determined.

Initial reaction-rate data analysis was carried out mainly to isolate the effect that Sn(IV) may have upon the equilibrium of Sn(II) based species.

Two weak points in our experimental procedure are:

- All the O₂ was assumed to be in solution; whereas some of it was in the gas phase above the liquid, mixed with water vapour and HCl.
- There was no agitation during the reaction.

Table III-3 shows the effect of varying amounts of O₂ on a 0.1M SnCl₂.2H₂O + 0.1M HCl solution. Note that for [O₂] > 0.029M, the reaction is independent of [O₂] and that for [O₂] < 0.0098M at 50°C consumption is practically quantitative.

From the four chemical species postulated by Walton[54] in relation to oxidation of Sn(II) due to U.V. absorption, the only one whose existence is not doubtful in the system under study is SnCl₃⁻.

Assuming the controlling kinetic step to be represented as 

\[-\text{oxidation} = k[\text{SnCl}_3^-]\]

the values of k for different solutions is shown in Table III-4. Figure III-4 shows a plot
of the Arrhenius equation for the previous reaction. A summary of the data is given in Table III-5.

One has to keep in mind that Sn(II) oxidation is an autoaccelerated reaction, hence the previous data which shows that chain initiation by SnCl₃⁻ is the controlling kinetic step is valid only for low [Sn(IV)].

### TABLE III-3

Effect of Oxygen Concentration Upon Sn(II) Oxidation

<table>
<thead>
<tr>
<th>Temperature °C</th>
<th>[O₂] 100 * molar</th>
<th>Time minutes</th>
<th>Final [Sn(II)] molar</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>0.49</td>
<td>15</td>
<td>0.099</td>
</tr>
<tr>
<td>30</td>
<td>0.98</td>
<td>15</td>
<td>0.097</td>
</tr>
<tr>
<td>30</td>
<td>2.91</td>
<td>15</td>
<td>0.095</td>
</tr>
<tr>
<td>30</td>
<td>9.74</td>
<td>15</td>
<td>0.096</td>
</tr>
<tr>
<td>30</td>
<td>29.4</td>
<td>15</td>
<td>0.096</td>
</tr>
<tr>
<td>50</td>
<td>0.49</td>
<td>10</td>
<td>0.099</td>
</tr>
<tr>
<td>50</td>
<td>0.98</td>
<td>10</td>
<td>0.098</td>
</tr>
<tr>
<td>50</td>
<td>2.91</td>
<td>10</td>
<td>0.091</td>
</tr>
<tr>
<td>50</td>
<td>9.79</td>
<td>10</td>
<td>0.088</td>
</tr>
<tr>
<td>50</td>
<td>29.4</td>
<td>10</td>
<td>0.089</td>
</tr>
</tbody>
</table>
Figure III-4
Plot of Arrhenius Equation
<table>
<thead>
<tr>
<th>Temperature °C</th>
<th>1000 * [SnCl$_5$] molar</th>
<th>Reaction Time minutes</th>
<th>100 * k minutes$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>2.37</td>
<td>15</td>
<td>2.92</td>
</tr>
<tr>
<td>30</td>
<td>5.37</td>
<td>15</td>
<td>3.04</td>
</tr>
<tr>
<td>30</td>
<td>9.01</td>
<td>15</td>
<td>2.94</td>
</tr>
<tr>
<td>35</td>
<td>2.13</td>
<td>15</td>
<td>5.02</td>
</tr>
<tr>
<td>35</td>
<td>7.86</td>
<td>10</td>
<td>5.1</td>
</tr>
<tr>
<td>40</td>
<td>2.07</td>
<td>15</td>
<td>8.81</td>
</tr>
<tr>
<td>40</td>
<td>7.43</td>
<td>10</td>
<td>9.05</td>
</tr>
<tr>
<td>45</td>
<td>2.03</td>
<td>10</td>
<td>16.52</td>
</tr>
<tr>
<td>45</td>
<td>7.1</td>
<td>5</td>
<td>16.24</td>
</tr>
<tr>
<td>50</td>
<td>1.99</td>
<td>5</td>
<td>29.36</td>
</tr>
<tr>
<td>50</td>
<td>6.81</td>
<td>5</td>
<td>29.57</td>
</tr>
</tbody>
</table>
TABLE III-5
Sn(II) Oxidation Summary of Data

<table>
<thead>
<tr>
<th>Temperature [°C]</th>
<th>k [minutes⁻¹]</th>
</tr>
</thead>
<tbody>
<tr>
<td>298</td>
<td>1.67*</td>
</tr>
<tr>
<td>303</td>
<td>2.96</td>
</tr>
<tr>
<td>308</td>
<td>5.06</td>
</tr>
<tr>
<td>313</td>
<td>8.93</td>
</tr>
<tr>
<td>318</td>
<td>16.38</td>
</tr>
<tr>
<td>323</td>
<td>29.47</td>
</tr>
</tbody>
</table>

#Extrapolated Activation Energy = 22018.7 cal/g mol

C. Sn(IV) Ion Hydration and Hydrolysis:

Stannic hydrates hydrolyze; the hydrolysis products aggregate. The aggregates are most likely mixtures of hydrates and hydroxides, and eventually precipitate losing hydration [55].

\[
e.g. \quad \text{Sn}^3+ (\text{H}_2\text{O})_2^2+ \rightarrow \text{Sn}^2+ (\text{OH})_2^- + 6\text{H}^+
\]

\[
m\text{Sn}^2+ (\text{OH})_2^- + n\text{Sn}^3+ (\text{H}_2\text{O})_2^2+ + m\text{H}_2\text{O} \rightarrow \text{Colloid}
\]

\[
\text{Colloid} - p\text{H}_2\text{O} \rightarrow \text{Precipitate}
\]

There is evidence [56] that the hydrolysis products and colloids have a wide range of specific gravities depending upon the degree of hydration; this has been the greatest obstacle in following the kinetics of the hydrolysis reaction. Due to the previously described limitation, we have to content ourselves with a very rough estimate of the speed of this reaction.
Intuitively, we assume that the amount of colloid and precipitate formed must bear some relationship to the amount of material hydrolyzed. Although this relationship is certainly a function of many other variables (temperature, pH, etc.) it gives an idea of the rate of hydrolysis.

The following is the experimental procedure used in following the hydrolysis reaction: Solutions of 0.1M SnCl$_4$.5H$_2$O in oxygen free water were placed in closed bottles. After certain test periods a bottle was opened, the solution stirred and then forced with pressurized N$_2$ through a 100 nm Nucleopore membrane in a colloid filtration cell. The filtrate was analyzed polarographically. The supporting electrolyte is known to redisperse Sn(IV) precipitates; hence any particles small enough to pass through the membrane were determined as Sn(IV) to provide an estimation of material not hydrolyzed.

From material balance considerations, whatever particles did not go through the membrane (referred to thereafter as "precipitate") were determined. The result, expressed as percent of material precipitated, is shown in Figure III-5.

D. Reaction Between Sn(II) and Sn(IV)

From our previous results, we know that hydrolysis products of Sn(II) if they exist do not affect this system.

It is known that Sn(IV) based precipitates can be redispersed for up to 48 hours at 23°C by adding small amounts of HCl and then agitating. This technological detail justified
Figure III-5

Precipitation of Sn(IV) as an estimate of its rate of hydration and hydrolysis.
preparing dispersions of Sn(IV) hydrolysis products of known concentration in the following manner.

One litre lots of 0.1M SnCl₂·5H₂O were left to hydrolyze and precipitate, then, when needed, were redispersed with magnetic stirring by the addition of 3 mL of HCl 36.5%. The dispersion was passed through a 100 nm Nucleopore membrane and analyzed polarographically to determine its concentration. Typically between 80 and 90% of the material was redispersed.

In a typical set of measurements, Sn(IV) hydrolysis product 0.084M was purged with zero grade N₂ for ten minutes; then 100 mL portions were transferred to bottles where 100 mL of SnCl₂·2H₂O + 0.1M HCl made with oxygen free water was added. The experiment was conducted at room temperature (approximately 23°C). One bottle was opened after each hour. A bulk sample of 0.5 mL was taken and analyzed; the remainder was filtered through a 100 nm Nucleopore membrane, and the filtrate was analyzed. All the analyses were polarographic.

The Sn(II) and Sn(IV) concentrations of the bulk samples were, within experimental error, the same as the original mixture (approximately 0.042M Sn(IV) and 0.05M Sn(II)). This indicated complete redispersion of the species in the supporting electrolyte.

The filtrates showed equimolar decrease in the concentrations of Sn(II) and Sn(IV). This evidence verified the one to one stoichiometry of the aggregated material.
The percentage of colloidaly-bound Sn(II) (that which did not go through the membrane) vs. time is shown in Figure III-6. This graph shows a very similar shape to the initial Sn(IV) hydrolysis-product precipitation (long induction period, followed by a linear region and finally a sudden acceleration). This indicates that this process may be unaltered by the presence of Sn(II) based species; and may indeed be controlled by the initial appearance of Sn(IV) based colloid.

This experiment does not indicate whether the Sn(II)-Sn(IV) reaction took place before Sn(IV) aggregation or after it formed a colloid. However we know that sensitizers perform optimally when they are yellow colloids; hence, we could assume that the production of active sensitizer is given by the rate of colloidal aggregation of Sn(IV) provided that enough Sn(II) is present to react with the Sn(IV).

It is also known that there are two mechanisms by which sensitizers become inoperative:

- Excessive colloid aggregation: It is expected that there is an optimum size of colloid for wetting and settling on surfaces. Once the colloids grow too large, aggregate and precipitate, surface coverage virtually stops.
- There is evidence that the Sn(II) bound to Sn(IV) continues to undergo oxidation to Sn(IV) in the presence of O₂. If the Sn(II)-Sn(IV) adduct is dried it does not oxidize in the solid state.
Figure III–6
Rate of Attachment of Sn(II) Ions To Colloidal Particles

Note: Circle diameters are not representative of error limits.
A proposed quantitative kinetic model for the production of surface active agent in the sensitizers is shown in a simplified form in Figure III-7. The factors controlling the production of the surface active agent are summarized in Table III-6.

**TABLE III-6**

Factors that Control the Formation of Surface Active Material

<table>
<thead>
<tr>
<th>Initial Composition</th>
<th>Controlling Factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sn(II)</td>
<td>Sn(IV)</td>
</tr>
<tr>
<td>Yes</td>
<td>No</td>
</tr>
<tr>
<td>Yes</td>
<td>Yes</td>
</tr>
<tr>
<td>Yes</td>
<td>Indifferent</td>
</tr>
</tbody>
</table>
Figure III–7  Model For The Production Of Surface Active Agent In Sn(II) Based Sensitizers
CHAPTER IV

ADSORPTION STUDIES

Adsorption measurements were performed mainly:

- To test the mechanistic model described previously.
- To evaluate quantitatively the effectiveness of the sensitizing systems.

Previously, sensitizer effectiveness has been evaluated using one of two techniques.

The percentage of area covered when using electroless plating is monitored in a given period (Pearlstein [57]). This process has the following drawbacks:

- It evaluates the product after surface preparation, sensitization, catalyst deposition and plating. If the deposit is not of good quality, one cannot be sure whether sensitization is the step that failed. The poor quality could have been caused by any of the other steps.

- It is only useful for distinguishing inferior deposits from deposits that appear relatively uniform so that no fine distinctions are made.

Feldstein and Weiner [58][59] studied the contact angle of several solutions on substrates as a function of ageing and composition. They drew several conclusions:

- The decrease of contact angle with ageing is not due to changes in surface tension.
- The ratio of Sn(II) to Sn(IV) ions is very significant. A plot of \([\text{Sn(II) / Sn(IV)}]\) vs. contact angle shows a minimum; an increase in Sn(IV) displaces the minimum to lower values.

- NaCl does not affect sensitizers that contain no Sn(IV), but reduces the contact angle of sensitizers that contain Sn(IV). The Sn(IV) ions "provide a new mechanism" for Sn(II) ions to get adsorbed.

- Feldstein and Weiner also propose the model of colloidal Sn(IV) ions surrounded by Sn(II) ions. More detailed description of the adsorption process is absent in the literature.

Contact angle determination has the advantage of being quick and simple but has a few disadvantages as well. It is hard to evaluate contact angle objectively; it is easier to compare material weight adsorbed per unit area than to compare angles. When in their period of greatest activity, the sensitizers tend to creep to the outside of the needle, making it difficult to place a drop of sensitizer of reproducible characteristics on the substrate. This measurement requires a reproducible substrate which by itself is a serious problem.

A. Experimental Procedure

Ottawa sand was passed through a fine sieve made of pantyhose to remove gross particulate matter. The sand was subsequently washed with water to float the dirt until the
water was uniformly gray and transparent. The sand was then washed three times with aqua regia for six hour periods. During this stage it was also stirred occasionally with a glass rod. The first time the aqua regia turned green; the next two times it stayed its characteristic red colour. Afterwards, the sand was washed for twenty four hours each, with concentrated and with dilute HNO₃. It was washed several times with distilled water, partially dried in an oven at 90°C, then washed again with distilled water which emerged transparent. This last procedure, that of partially drying and then rinsing, was repeated several times until the water in contact with the sand was approximately at a pH level of four. Finally, all water was evaporated at 90°C, and subsequently the sand was dried at 150°C overnight.

The final product after the cleaning process was essentially, pure white silica. By volume displacement, it was found to have a specific gravity of 2.625 (2.65 is the theoretical value for pure β-SiO₂ [60]). A sample of 240.3 g was subjected to a sieve analysis. This provided the particle size distribution and the specific area. This sand sample was not, however, used in the adsorption studies due to possible contamination during sieving analysis.

In this experiment the sand grains were assumed to be nonporous spheres since sand grains are known to have a very low density of very small pores, approximately 4nm [61]. The
specific surface, as given by the distribution shown in Table IV-1 and Figure IV-1, is 133.01 cm²/g

**TABLE IV-1**

Sieving analysis

<table>
<thead>
<tr>
<th>Sieve Range</th>
<th>Average Radius (mm)</th>
<th>Specific Volume (mm)³/g</th>
<th>Specific Area (mm)²/g</th>
<th>% Total Area</th>
</tr>
</thead>
<tbody>
<tr>
<td>-28 +48</td>
<td>0.225</td>
<td>14.78</td>
<td>197.1</td>
<td>1.48</td>
</tr>
<tr>
<td>-48 +60</td>
<td>0.1375</td>
<td>69.16</td>
<td>1508.98</td>
<td>11.34</td>
</tr>
<tr>
<td>-60 +100</td>
<td>0.1</td>
<td>180.63</td>
<td>5418.88</td>
<td>40.74</td>
</tr>
<tr>
<td>-100 +115</td>
<td>0.0675</td>
<td>68.58</td>
<td>3047.87</td>
<td>22.91</td>
</tr>
<tr>
<td>-115 +200</td>
<td>0.04875</td>
<td>45.91</td>
<td>2825.00</td>
<td>21.24</td>
</tr>
<tr>
<td>-200</td>
<td>0.01875</td>
<td>1.90</td>
<td>303.24</td>
<td>2.28</td>
</tr>
</tbody>
</table>

Total 13301.07 100%

Fifty mL of the sensitizer was added to 10 g of sand and stirred in a beaker for 10 minutes. The sand was then filtered, using soft suction with a Buchner filter, and washed with distilled water. The filtrate (sensitizer and washing waters) was saved. Sand and filtrate individually were added to 50 mL of aqua regia. The sand was stirred with the aqua regia for ten minutes, then filtered and washed. The aqua regia solutions plus washing waters were retained. At this stage one filtrate contained the Sn that was adsorbed onto the
Figure IV-1: Sand Grains Size Distribution
sand, while the other contained the part that was not adsorbed. Both filtrates were boiled under the hood. This procedure had three objectives:

- To oxidize all Sn to Sn(IV).
- To oxidize the HNO₃ to nitrogen oxides (left to evaporate).
- To reduce the volume to less than 100 mL.

After boiling, the filtrates were transferred to 100 mL volumetric flasks, and their volume was topped up to 100 mL by the addition of distilled water. One mL of this aliquot was added to 200 mL of supporting electrolyte (1M HCl + 4M NH₄Cl + 0.005% gelatin) and analyzed polarographically for Sn(IV).

The total Sn in sensitizer was required to equal the Sn adsorbed plus Sn not adsorbed within plus-minus 5%. If measurements were outside this range they were considered unreliable, eliminated from further analysis and not reported. The procedure is shown diagrammatically in Figure IV-2.

In this dissertation, the quantity of adsorption will be referred to equivalent elemental metal (Sn or Pd respectively).

B. Effect of Contact Time on Adsorption

The silica was stirred for ten minutes while in contact with the sensitizer. Because the sensitizer is a dynamic system, the contact time must be short enough to prevent significant changes in the sensitizer, but long enough to permit the laboratory procedures needed for reproducible
Figure IV-2. Procedure For Adsorption Quantification
results. A contact time of ten minutes was found to be a reasonable optimum.

From adsorption studies on other systems [62], a practical approach to equilibrium adsorption may require a relatively long time (e.g., 48 hours). Little is known, however, about the kinetics of adsorption of Sn-based sensitizers onto any substrate.

Literature from industrial processes for the plating of plastics [63] gives a wide range (from 2 to 30 minutes) for the material contact time with the sensitizer.

Despite the limitations of Sn-based sensitizers as adsorbents, it was decided to use a slow changing sensitizer, 0.1M Sn(II) + 0.1M HCl, which had been aged five days in a closed bottle at room temperature. To this sensitizer, 10 mg/L of hydroquinone were added after the fifth day of ageing, just prior to the adsorption experiments. The silica was brought in contact with the solution for intervals of 2, 10, 50, and 250 minutes. The results shown in Figure IV-3 illustrate that the adsorption process is relatively fast. Since the kinetics of the adsorption process is a function of many variables a general statement can not be made about how close to the adsorption plateau different sensitiser systems will be in ten minutes. It is postulated that the species which gets adsorbed is fairly linear, since it is known [64] that linear chains, even those with a high molecular weight, exhibit very fast kinetics of adsorption. They behave like adhesives. A
Figure IV–3. Adsorption As A Function Of Time
relatively small density of branching slows the adsorption process considerably.

C. **Effect of Surface Active Agents**

Early attempts to explain the performance improvement of Sn(II) based sensitizers upon the addition of Sn(IV), suggested that the latter acts as a wetting agent, allowing the Sn(II) to get attached to the surface, while the Sn(II) is still the responsible agent for the catalyst reduction. Marton and Schlesinger [65] employed electron microscopy studies to show that the addition of a wetting agent such as Kodak "photo flo" to a freshly prepared Sn(II) sensitizer had about the same effect as ageing Sn(II) for a week. It increased by an order of magnitude the density of nucleation sites as compared to fresh pure sensitizer.

In the literature, very few practical sensitizer formulations do include wetting agents.

The mechanistic model described previously assumes that the adduct, responsible for the sensitizing activity, is itself surface active. Hence, another surface active agent would be a cosurfactant, and the system would be expected to behave according to theories developed regarding adsorption of mixtures of surfactants [66]. To test this statement the following experiment was performed.

Stock solutions of 0.2% by weight of the surface active agents sodium dodecyl sulfate (SLS) and Triton X-100 were prepared. From zero to one hundred mL of these solutions in
increments of 10 mL were added to 50 mL of sensitizer, transferred to a 200 mL volumetric flask, and topped to a level of 200 mL by the addition of distilled water. Fifty mL of this solution was used for the adsorption measurements, and the rest was discarded. The sensitizers used were 0.1M Sn(II) + 0.1M HCl, freshly prepared and aged for 10 days in a closed glass bottle at room temperature. The results are shown in Figures IV-4 and IV-5.

In the case of the freshly prepared sensitizer, all surface active agents caused an increase of the amount adsorbed. This occurred in a nearly linear fashion with the concentration of the surfactants. Note that the sensitizer by itself was not adsorbed. Even with the highest surface active concentrations studied, the adsorption is much lower than with the pure aged sensitizer. Furthermore, by extrapolation from the curves, it is not expected that a high concentration of surface active materials will yield a sensitzer with high adsorption characteristics. Consider also the fact that at 0.01% by weight, these materials cause only slight foaming, though at 0.1% the foaming increases dramatically. Because of these characteristics, it is doubtful that these surfactants could be used in a production environment.

In the case of the aged sensitizer, the results were as expected. The SLS, an ionic surfactant, with increased concentration competes with the sensitizer for the adsorption area available. Hence the adsorption of the sensitizer
Figure IV-4. Effect Of Surface Active Agents
Figure IV-5. Effect Of Surface Active Agents
decreases. With Triton X-100, which is nonionic, we notice a peak where the adsorption increases. This peak is confirmed by another set of measurements directed at enlarging the area. These results are shown in Figure IV-6. A nonionic surfactant also competes for adsorption area, but it increases the dielectric constant of the media allowing for tighter packing as well. This effect is responsible for the peak. With increased concentration, the area competition overpowers the electrostatic effect. At its maximum, the peak represents less than 10% of adsorbed Sn over pure sensitizer.

Since the range of the peak is narrow, and because there are inherent analytical difficulties in tracking another component in a solution, it is safe to conclude that the addition of surface active agents is an investment which yields minimal return.
Figure IV-6. Adsorption Peak Expanded
D. Factors that Affect the Kinetics of Oxidation of Sn(II)

The formation of the surface active material which is responsible for the sensitization process is the result of a series of reactions. The first step, for sensitizers initially containing Sn(II) only, is the oxidation of Sn(II) to Sn(IV). It is expected that the factors which influence the kinetics of this oxidation will determine the effectiveness of the reaction and the time period during which the sensitizer is useful.

Figure IV-7 shows the adsorption vs. time relationship for two sensitizers made with 0.1M Sn(II) + 0.1M HCl and 0.1M Sn(II) + 0.5M HCl. The higher HCl concentration accelerates the oxidation of Sn(II). It also yields a sensitizer that matures faster, has a greater adsorption maximum and a shorter effectiveness period than the lower HCl concentration. A similar effect is demonstrated in Figure IV-8 for the adsorption behaviour of a sensitzer made with 0.1M Sn(II) + 0.1M HCl to which 10 mg/L of thiourea and 10 mg/L of hydroquinone were added — an accelerator and an inhibitor respectively. The sensitzer with the inhibitor did not mature during the period of observation.

Sensitizers made with 0.1 to 1.0M Sn(II) chloride (in increments of 0.3M) + 0.1M HCl were studied. Their adsorption maxima and induction times were approximately equal, but the effectiveness period varied between 5 and 20 days for the lowest and highest concentrations, respectively. In these
Figure IV–7. Effect Of HCl
Figure IV–8. Effect Of Oxidation Accelerator And Inhibitor On Sensitizer Adsorption.
cases, the oxidation of Sn(II) is the limiting factor in the production of surface active material. The longer activity period occurs because there is continuous production of surface active material. This material is responsible for adsorption, whose concentration apparently reaches steady state (until the reactant is exhausted). Of course this behaviour takes place only as long as the oxygen in the air is allowed into the solution. One could also try to influence the extent of the oxidation of Sn(II) by preventing the free arrival of oxygen into the solution.

E. Factors that Affect the Reaction Between Sn(II) and Sn(IV)

The general results of this research show that the assumption of adding Sn(IV) to a Sn(II) based sensitiser will improve performance is correct. The question is: should one skip a step in the chain reaction that produces the surface active agent? There seems to be no reason to wait for the Sn(II) to be oxidized to Sn(IV). Although the oxidation is very easy to accelerate, it is unclear at present how to control it, and the quantitative effects of accelerators are irreproducible. This is the reason why oxidation is seldom accelerated intentionally.

The direct mixing of Sn(II) and Sn(IV) is also problematic because of the autoaccelerating nature of the oxidation reaction. When mixing stoichiometric amounts of Sn(II) and Sn(IV) solutions in hydrochloric acid, the yellow
colour characteristic of the reaction product between Sn(II) and Sn(IV) starts to appear between 20 minutes and 2 hours at room temperature, depending on HCl concentration. This is based upon observations here which conflict with reports of other researchers [67].

Analysis of the stoichiometrically Sn(II)-Sn(IV) solutions without O₂ exclusion reveals that Sn(II) disappears faster than Sn(IV). The Sn(IV) also eventually disappears through precipitation of hydrolysis products not through reaction with Sn(II). Although this pattern of behaviour is reproducible qualitatively, quantitative concentration vs. time curves for Sn(II) and Sn(IV) are not. When mixing Sn(II) and Sn(IV), consider that the reaction between Sn(II) and Sn(IV)-based products is relatively fast compared to the formation of Sn(IV) hydrolysis products. Since oxidation of Sn(II) is accelerated by the excess of Sn(IV), the result is that far less surface active agent gets formed than is expected from stoichiometry.

Bubbling the water used in preparing the solutions with N₂, and blanketing the solutions and the mixture for a few minutes to prevent air from getting in avoids the problem of Sn(II) oxidation. Unfortunately, this process may not be economical in an industrial environment.
Attempts to optimize the formation of Sn(II)-Sn(IV) product by adding Sn(IV) in less than stoichiometric amounts have been fruitless, mainly due to the irreproducible nature of the autoaccelerated oxidation of Sn(II).

The only practical way to optimize the formation of the Sn(II)-Sn(IV) product was the addition of small amounts of hydroquinone to the Sn(II) solution. Hydroquinone is a retarder of the oxidation.

The reason for all the effort towards optimising the formation of the Sn(II)-Sn(IV) product is that this product is either the precursor of the surface active agent or the agent itself.

The adsorption vs. time behaviour of 0.1M Sn(II) + 0.1M Sn(IV) + 0.1M HCl + 10 mg/L of hydroquinone is shown in Figure IV-9. Note that the initial adsorption is much higher than in the pure Sn(II) cases, but also that the sensitizer still requires some maturing time to yield maximum adsorption. This is to be expected, since the Sn(II)-Sn(IV) product has to aggregate to achieve an optimum chain length for adsorption. This happens through the hydrolysis of Sn(IV), which is the limiting step in the process.

"For the remainder of this section, "Sn(II)-Sn(IV)" will refer to the adduct formed between Sn(II) and all Sn(IV) species, including hydrolysis-products, as long as they are not precipitates."
Figure IV–9.
Adsorption Of Sn(II) + Sn(IV) Sensitizer With Inhibitor
Another point to note is that these sensitizers have very short lifetimes and very sharp drops in activity.

Behaviour with respect to maximum of adsorption and lifetime of the sensitizers are independent of the concentration of the Sn(II)-Sn(IV) adduct as long as the concentrations of both Sn(II) and Sn(IV) are greater than approximately 0.005M. Note that this discussion is limited to 50 mL of sensitizer in contact with 0.13 m² of substrate. Of course, if the substrate area is increased, the figures will change. This figure gives us a starting point to estimate maximum bath loading.

Behaviour with respect to maximum adsorption particularly can be explained in terms of the surface approaching saturation*. No explanation is available for the lifetime of the sensitizer, since so far there is little knowledge about the growth mechanism of the surface active chain.

The previous results suggest that optimising the Sn(II)-Sn(IV) compound will not yield better deposits**, but that it will maximize the amount of area sensitized before sensitizer exhaustion.

*When in their optimum, all the sensitizers present very similar adsorption values.

**Assume bath loading is well below maximum allowable.
F. **Substrate Effect**

After the original batch of silica was processed, a 25 Kg. bag of the finest grade available Ottawa sand was obtained in order to continue the experiments. Large amounts of this sand were sieved to isolate fractions -115 +200 mesh for use. This silica corresponded to an average radius of 0.04875 mm and a specific area of 1615.4 cm²/gr., based on the same assumptions that were followed for the first batch of sand. This sand was cleaned in steps which imitated the procedure used for the first batch of sand. The objective was to create reproducible surface conditioning. The only intentional difference between the two silica samples was the grain size distribution. This however is not expected to have any effect upon the adsorption, since the silica grains must be at least two orders of magnitude smaller than they are before curvature effects become significant.

To test the new substrate, a sensitizer used with the previous silica was prepared, and the adsorption was measured 0.1M Sn(II) + 0.1M HCl aged for 5 days. Conditions and procedure were identical to the one used to evaluate the effect of contact time on adsorption. Due to the higher specific area of this batch, only 1 g of silica was used as compared to 10 with the previous experiments.

The adsorption was 1946.9 g/m² as compared to 1682.5 g/m² for the previous silica. That difference is approximately 15% based on the first batch, which can be explained in terms of
shape factors or random nature. We must also consider the possibility that the error is due to the poor characterization of the substrates.

Silica is supposed to be attacked very slowly by neutral and basic aqueous solutions, but not by acidic ones (with exception of the ones containing HF or fluorides [68]). Hence, the cleaning procedure must have removed all previously adsorbed impurities, with the exception of gases, without attacking the silica (not creating either pores or functional groups on the surface). It is concluded that the surface differences between the two batches of silica were already present before the cleaning, even when both sands were supposedly mined in the same region.

6. Effect of Breaking the Colloid

According to the mechanistic model, one of the reasons why sensitizers stop working is that the surface active chain continues to grow until the surface activity ceases, and/or, the chain solubility in water goes on decreasing with growth, until it phase separates and forms the colloid, (which also grows until it precipitates). Whether the chain is surface active to the onset of precipitation, or if the activity ceases before precipitation is not known.

There seems to be no reason why the surface activity could not be restored if the overgrown colloids and precipitates are broken into chains of adequate length. To test this, a 0.1M Sn(II) + 0.1M HCl sensitizer was aged in an
accelerated fashion by heating it to 70°C for one hour. After cooling, the sensitizer phase separated completely into an yellow turbid layer, with the transparent material on top.

The metallization of glass slides was attempted with the previously described sensitizer. The results were negative, thus indicating the cessation of effectiveness.

The sensitizer was shaken and 200 mL portions were poured into 250 mL beakers. Each beaker was sonified continuously for a different time period with a Sonic 300 Dismembrator (Artek systems) set at 60% instrument power. The tip of the emitter was kept 2 cm below the surface level. The adsorption was measured right after sonification, and at periods of 48 and 96 hours, to provide the results shown in Table IV-2.
TABLE IV-2

Adsorption of Sonified Sensitizers

[=] mg/m²

<table>
<thead>
<tr>
<th>Time After Sonification</th>
<th>Sonification Time</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Immediately</td>
</tr>
<tr>
<td>10 Seconds</td>
<td>136</td>
</tr>
<tr>
<td>30 Seconds</td>
<td>854</td>
</tr>
<tr>
<td>1 Minute</td>
<td>1386</td>
</tr>
<tr>
<td>3 Minutes</td>
<td>Coagulated</td>
</tr>
</tbody>
</table>

Glass slides were metallized using the sensitizer right after sonification. The acidic electroless Ni described by Marton and Schlesinger [69] was employed. This bath renders bright smooth deposits when used with any other active sensitizer. In this case, the uniform coverage deposits were dull black, and did not have a smooth aspect. The deposit was improved somewhat by filtering the sensitizer.

From this experiment it is concluded that:

- Sensitizer activity can be restored by mechanically breaking the colloid.
- The sonified sensitizer contains coarse material. This material has a long range effect, causing roughness in the final deposit.
- Amount of shearing is critical: too little does not regenerate the sensitizer effectively, too much coagulates it.
The regenerated sensitizer is short lived, probably due to capture of shorter chains and small colloids by coarse particles.

H. Adsorption of Non-Sn Based Sensitizers

There are many metal salts which precipitate into a disperse phase forming a colloid, upon pH changes or by addition of another substance. Analogy with the mechanism of formation of other colloids by dispersion [70] suggests that in the cases that do not involve reaction of the metal salt, the salt forms oligomeric chains which grow and eventually precipitate in a similar fashion to the Sn(II)-Sn(IV) product. Hence, it is expected that at some point this chain may also be surface active, and that if the metal involved can be oxidized and in so doing can reduce a noble metal, a sensitizer is obtained.

This mechanism does not imply that all sensitizers work this way, but provides a model for the search for new sensitizers. Neither is the mechanism restricted in principle to polivalent metal salts. It should also work with powerful reducing agents which follow the previously described behaviour. Since most of our chemical experience is with polivalent metal salts, this work will concentrate on them.

Feldstein has a patent [71] in which electroless deposition is done without sensitization nor catalyst treatment. The process involves immersing the substrate in mixtures of salts, and then immersing it in very strong
reducing agents (based on $\text{N}_2\text{H}_4$ or aminoboranes). The Fehling reagent also works without sensitization, but the deposit has no adherence.

We have observed direct reduction of Co onto glass without sensitization and catalyst deposition when we have added H$_2$O$_2$ to NH$_3$-based, electroless Co plating solutions. The partial oxidation of NH$_3$ to N$_2$H$_4$, which is a strong reducing agent, is a possible explanation:

$$2\text{NH}_3 + \text{H}_2\text{O}_2 \rightarrow \text{N}_2\text{H}_4 + 2\text{H}_2\text{O}$$

Since Co-based catalysts are used in the industrial production of N$_2$H$_4$ by partial oxidation of NH$_3$ [72]. A similar plating, although less reproducible, can be observed by neutralizing NH$_3$-based electroless Cu with excess H$_2$SO$_4$. In this procedure, shiny spots of Cu get plated. They start bubbling immediately and are dissolved very quickly by the action of the acid. A reference is made by Goldie to a British patent [73] for aerosol deposition, which mixes two solutions: Solution A. CuO 10 mg/L + (NH$_4$)$_2$SO$_4$ 30 g/L + NH$_4$OH 25 mL/L. Solution B. H$_2$SO$_4$ 5 g/L. They theorize that aqueous solutions of cuprous salts are stable only when suitably complexed, and for that an acidic media is required. They also propose a mechanism for the deposition based on the disproportionation of the cuprous ion:

$$\text{Cu}_2\text{O} + 2\text{NH}_3 + 2\text{NH}_3 \rightarrow 2[\text{Cu(NH}_3)_2]^+ + \text{H}_2\text{O}$$

$$[\text{Cu(NH}_3)_2]^+ + 2\text{H}^+ \rightarrow \text{Cu}^+ + 2\text{NH}_4^+$$

$$2\text{Cu}^+ \rightarrow \text{Cu}^{2+} + \text{Cu}^0$$
All the previous observations prove the fact that under certain conditions metal salts can be adsorbed onto different substrates in such amounts that with a strong enough reducing agent an adherent continuous film can be obtained.

A system was discovered accidentally while we were developing a formaldehyde-based electroless-Fe plating solution. The Na-formate was added to a FeSO₄ solution. The yellow-greenish solution turned cloudy, and, in a matter of minutes, formed a ring on the beaker at the air solution interface. Such a ring is typical of colloidal coagulation and is similar to the one formed by long standing Sn(II)-based sensitizers. This ring was very hard to scrape even with fiber, and when dry it showed iridescent colours when viewed against light. This was possibly associated with a narrow size distribution of the colloid, and when coagulated it packed into a diffraction grating-type structure. This solution was tested as a sensitizer with PdCl₂ solution as a catalyst and with an electroless Ni bath. The uniformity of the deposit proved it to be an excellent sensitizer.

Although all the previously described systems offer great potential, the one that was selected for a more detailed study is based on PdCl₂. This salt used with dilute HCl is the catalyst most widely used after sensitization. Pearlstein[74] found that electroless Ni can be deposited onto polystyrene that has had PdCl₂ treatment without previous sensitization.
His results extracted from Goldie [75] are summarized in Table IV-3.

<table>
<thead>
<tr>
<th>pH of PdCl₂ Solution</th>
<th>Percentage Area Coated With Ni at 27°C</th>
<th>43°C</th>
<th>52°C</th>
<th>74°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.0</td>
<td>0</td>
<td>0</td>
<td>2</td>
<td>10</td>
</tr>
<tr>
<td>3.4</td>
<td>0</td>
<td>15</td>
<td>25</td>
<td>100</td>
</tr>
<tr>
<td>3.8</td>
<td>0</td>
<td>99</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>4.4</td>
<td>40</td>
<td>99</td>
<td>100</td>
<td>100</td>
</tr>
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<td>4.8</td>
<td>90</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>5.8</td>
<td>0</td>
<td>2</td>
<td>5</td>
<td></td>
</tr>
</tbody>
</table>

Concentration of PdCl₂ = 0.1 g/L

Using glass slides as substrate, we were fairly successful in reproducing Pearlstein's findings. Two of this system's peculiarities that could not be fully explained were the motivation for a more detailed study of the system:

- In this system, as opposed to the others, there is nothing applied before or after the PdCl₂ to reduce it to the metallic state. How, then, is it reduced? If the Pd is not in the metallic state, how was the electroless Ni deposition initiated? It is not conceivable that the chloride initiated the deposition itself. Although the
contact potential between glass and liquid solutions can in some cases be large enough to reduce a noble metal like Pd, we are not aware of any case in the catalyst preparation literature where Pd is deposited merely by contacting clean silica (or any other substrate) with a Pd salt. (Silica has been used extensively as support for Pd-based catalysts).

- Although deposit uniformity is not a measure of the nucleation density, the experience here when Sn-based sensitization is used indicates that if the deposit is very uniform and covers the edges while still semi-transparent to the eye, the final deposit will be highly adherent, meaning of a relatively high nucleation density. Using PdCl₂ without any sensitization, the uniformity is excellent when still semi-transparent, but the final deposit has poor adherence. It can be wiped off with the finger even when dry.

The pH of acidic PdCl₂ catalysts is between 0 and 1. The method of Pearlstein to control the pH was ignored. In other research done along these lines [76], the pH was controlled by careful additions of NaOH, which is equivalent to having very small amounts of HCl and NaCl. This practice was difficult and a more conventional buffer was preferred. From the many buffering systems described in the literature, one using K-acid-phthalate and HCl or NaOH for the range pH 4 to 6 (Shugar [77]) was used.
The adsorption measurements followed the procedure previously described for Sn based sensitizers.

The supporting electrolyte for the polarographic determination of Pd was 0.1M ethylenediamine + 1M KCl + 0.005% methyl red (as maxima suppressor).

Figure IV-10 shows the adsorption vs. pH curve at room temperature for a 1.0 g/L PdCl₂ + 0.1 M HCl, buffered with the system previously mentioned. Note that the optimum pH is around 5, dropping faster towards basic than towards acidic.

PdCl₂ is highly soluble in water at high and low pH values. Solubility is reduced in the intermediate pH region of 6-11. Therefore, under a wide range of conditions, a disperse phase is formed when a solution is brought inside this pH range.

The concentration of the materials compounding the buffer system is much higher than the concentration of PdCl₂. When the buffering solutions are moderately diluted, they maintain the pH. It is the regulating capacity which decreases.

Table IV-4 shows the effect of diluting the buffer upon adsorption. Note that decreasing the amount of foreign salts causes a small increase in the adsorption, but the pH is more difficult to control.
Figure IV–10. Adsorption Of Pd(II)
### TABLE IV-4

**Effect of Buffer on Adsorption**

<table>
<thead>
<tr>
<th>Buffer</th>
<th>X⁺</th>
<th>0.75X</th>
<th>0.50X</th>
<th>0.25X</th>
<th>X⁻⁺</th>
</tr>
</thead>
<tbody>
<tr>
<td>Adsorption</td>
<td>150.5</td>
<td>154.0</td>
<td>161.7</td>
<td>168.1</td>
<td>82⁻⁻</td>
</tr>
</tbody>
</table>

+ "X" is a buffer stock solution made of: 500 mL 0.1M potassium hydrogen phthalate + 225 mL 0.1M NaOH.

++ After Sn-based sensitization.

* Average of three measurements.

Also shown in Table IV-4 is the adsorption behaviour of Pd on a silica that was stirred in a Sn-based sensitizer (0.1M Sn(II) + 0.1M HCl aged for five days) for ten minutes, filtered, rinsed with water and dried.

The amount of Pd salt adsorbed is smaller in sensitized than in pure silica, which was unexpected. This also opens another field for research: the need to determine the loci of Pd adsorption.
CHAPTER V

TEM STUDIES

The objectives of the TEM studies were:

- To quantify the relationship between the adsorption of sensitizers and the density of nucleation sites which they produce.

- To establish whether there is any relationship between the adsorption of sensitizers and the size of crystallites in the electrolessly deposited film.

Ideally, the density of nucleation sites should be quantified right after catalytic deposition. In practice it is very seldom that a TEM sample which will survive the electron beam long enough will also have the required resolution to allow a photograph to be taken. A photograph of one such sample is shown in Figure V-1. Instead, a metal is electrolessly deposited for a set amount of time, before determining the island size distribution and counting the density of metal islands. This is an imperfect procedure, since only a small portion of the catalyzed nuclei is initiated and develops to become metal islands. Most of the catalytic nuclei are covered by the metal film. One should also remember that initiation of nuclei growth is a probabilistic process; hence island density and island size distribution will vary with time in the metallizing bath. Another issue to consider is that the probability of nuclei
Figure V-1. Substrate After Catalyst

Figure V-2. Electrolessly Plated Substrate
growth is a function of the wetting properties of the metallizing bath (and, to a lesser degree, of the flow pattern). Figure V-2 is a schematic of the island growth process. Although simplified, the drawing shows a very complex five phase system. To illustrate the point, consider an $H_2$ bubble before it is dislodged and replaced by a new growing bubble. It is plain that $H_2$ hinders the solution from reaching the substrate.

Metallizing baths do not operate at a steady state. The industrial and laboratory reasons for this are of completely different nature. Consider the specific case of Ni-P alloys. In industry, a bath undergoes an average of fifteen replenishment cycles before being discarded. This is usually limited by the amount of phosphites that can be dissolved, hence, the accumulated phosphites and breakdown products of complexing agents, surfactants, etc. affect the wetting properties of the bath. In the laboratory the most reproducible solutions are acidic. Unfortunately, the crystallites produced in acidic baths are so small that it is very difficult to study them. On the other hand, almost all alkaline baths we know undergo ammonia evolution. Working with open beakers, there is no condensation and recirculation of these vapours; therefore pH control is not practical.

According to statistical Tables [78], in order for the experimental distributions (island and crystallite sizes) to be within confidence levels of 95 or 99% of the actual
distributions, the number of islands and crystallites to be sized is in the several thousands. Taking the number of photographs to obtain these sampling sizes is prohibitive in terms of cost and analysis time; therefore, this work proceeded with the following limitations.

- The number of islands in each individual picture ranges between 200 and 2000 (in dark field micrographs between 50 and 500 crystallites). In most cases only one picture was used to derive the distribution.

- "Large" areas with no islands were excluded in calculations of island density. This topic is discussed later under "clustering".

- The magnifications used in our calculations are panel readings. No calibrations were done on the TEM. Due to very large hysteresis effects of electromagnetic lenses, the magnification and camera lengths vary each time power to the lenses is turned on. In this case that means each time the microscope is used. This introduces an uncertainty of approximately plus-minus 10%.

A. Experimental

TEM samples were prepared as described in Appendix D. The supporting film of the samples was given the treatment shown in Figure V-3. The two deposition times shown correspond to: i) very early stages of nuclei growth and ii) when Ni-P islands cover between 60% of the surface and continuous film.
Sensitize 10 minutes

Water rinse 1 minute

Catalyze 2 minutes

Water rinse 1 minute

Plating bath 10 and 60 seconds

Eleven sensitizers

Twenty-two sample types

Figure V–3. Variety Of Samples
The catalyst solution and electroless Ni bath used are described in Tables V-1 and V-2.

TABLE V-1  
Catalyst Solution

<table>
<thead>
<tr>
<th>Component</th>
<th>Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>PdCl₂</td>
<td>0.1 g/L</td>
</tr>
<tr>
<td>HCl (12M)</td>
<td>0.1 mL/L</td>
</tr>
<tr>
<td>H₂O</td>
<td>balance to 1 L</td>
</tr>
<tr>
<td>Temperature</td>
<td>23°C</td>
</tr>
</tbody>
</table>

TABLE V-2  
Electroless Ni Bath

<table>
<thead>
<tr>
<th>Component</th>
<th>Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>NiSO₄.6H₂O</td>
<td>32.0 g/L</td>
</tr>
<tr>
<td>NH₄-Citrate</td>
<td>100.0 g/L</td>
</tr>
<tr>
<td>NH₄Cl</td>
<td>1.0 g/L</td>
</tr>
<tr>
<td>NaOH</td>
<td>2.2 g/L</td>
</tr>
<tr>
<td>Triton X-100</td>
<td>0.1 g/L</td>
</tr>
<tr>
<td>Na₃PO₂.H₂O</td>
<td>40.0 g/L</td>
</tr>
<tr>
<td>H₂O</td>
<td>balance to 1 L</td>
</tr>
</tbody>
</table>

*Added immediately before use  
Temperature 23°C

Eleven sensitizers were used, as listed in Table V-3. These sensitizers cover most of parameters varied in the
adsorption studies and for which the results correspond to a wide range of adsorption values.

**TABLE V-3**

<table>
<thead>
<tr>
<th>Sensitizer</th>
<th>(0.1\text{M SnCl}_2\cdot2\text{H}_2\text{O} + 0.1\text{M HCl})</th>
<th>Ageing [h] Hours</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td></td>
<td>0</td>
</tr>
<tr>
<td>II</td>
<td>0.05% Triton X-100 (weight)</td>
<td>0</td>
</tr>
<tr>
<td>III</td>
<td>0.05% Triton X-100 (weight)</td>
<td>240</td>
</tr>
<tr>
<td>IV</td>
<td></td>
<td>48</td>
</tr>
<tr>
<td>V</td>
<td></td>
<td>96</td>
</tr>
<tr>
<td>VI</td>
<td></td>
<td>144</td>
</tr>
<tr>
<td>VII</td>
<td></td>
<td>288</td>
</tr>
<tr>
<td>VIII</td>
<td>10 mg/L Thiourea</td>
<td>24</td>
</tr>
<tr>
<td>IX</td>
<td>10 mg/L Thiourea</td>
<td>72</td>
</tr>
<tr>
<td>X</td>
<td>10 mg/L Hydroquinone</td>
<td>3</td>
</tr>
<tr>
<td>XI</td>
<td>10 mg/L Hydroquinone</td>
<td>48</td>
</tr>
</tbody>
</table>

From each TEM sample three photographs were attempted: Bright field, selected area diffraction and dark field. In some cases there was not enough intensity in the dark field mode to observe an image. In those cases, results were complemented by using diffraction pictures.
Dark field and diffraction modes were used for the purpose of estimating crystallite size. Dark field lights directly the crystallites. From a diffraction pattern, the peak width at half peak height (above the base line) is inversely proportional to the number average crystallite size when ring broadening is due to crystallite size only. Ring broadening is considered by some researchers [79] as the last resort by which to estimate crystallite size, since there are many other factors that may contribute to this broadening. The most important factor which affects ring broadening in this case is probably stresses within the deposit. If the broadening is solely due to crystallite size, the width at half peak height should be the same for all rings but this was found not to be the case. When ring broadening is employed, a single ring is used. This ring was calibrated first using different samples where dark field image was also available.

When no image is obtained using dark field, it is because the diffraction rings are of "low" intensity, diffuse and hence difficult to resolve (mainly because of (i) very small amounts of material present and/or (ii) low crystallinity). The radial intensity of one such pattern is shown in Figure V-4.

To overcome the previous problem, overexposing the film was

- Not exactly. The real number average is slightly smaller, since we really size the shadow the crystallite produces by blocking electrons. The crystallite orientation sometimes leads to shadow which is bigger than the crystallite.
tried when obtaining diffraction patterns. Figure V-5 shows the radial intensity of one set of overexposed patterns. Seldom did the technique of overexposing of diffraction pattern help. This is due to irregularities in the film response, in which, very high electron beam intensity causes smearing to occur on the photographic film.

The use of electroless Cu deposits instead of electroless Ni was tempting, since the Cu deposits give high intensity in dark field and well defined rings in the diffraction patterns. The radial intensity of one Cu diffraction pattern is shown in Figure V-6. Studies with Cu did not continue because the deposits were not uniform at a microscopic scale, the technological knowledge of Ni-P is more advanced than for Cu.

The negatives were digitalized and analyzed with a computerized image processing system described in Appendix E.

B. Results

Table V-4 lists the mean island size and standard deviation for the samples. The islands were considered as half spheres. As expected the distribution is narrower in the early stages of growth than in the later ones. Note that sensitizers corresponding to higher levels of adsorption yield a smaller average sized island and less broadening of the size distribution with time of deposition than the sensitizers corresponding to lower levels of adsorption. The effects can be appreciated more in Figures V-7 and V-8 where the island size distributions for films prepared with
Figure V–5. Series Of Overexposed Diffraction Patterns
Figure V–6. Electroless Cu Diffraction Peaks
<table>
<thead>
<tr>
<th>Sensitizer</th>
<th>Time in Plating Bath [s]</th>
<th>Diameter Average [nm]</th>
<th>Standard Deviation [nm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>60</td>
<td>140.6</td>
<td></td>
</tr>
<tr>
<td>II</td>
<td>10</td>
<td>17.1</td>
<td>2.3</td>
</tr>
<tr>
<td>II</td>
<td>60</td>
<td>95.3</td>
<td>17.8</td>
</tr>
<tr>
<td>III</td>
<td>10</td>
<td>&lt; 1</td>
<td></td>
</tr>
<tr>
<td>III</td>
<td>60</td>
<td>4.9</td>
<td>1.1</td>
</tr>
<tr>
<td>IV</td>
<td>10</td>
<td>6.3</td>
<td>&lt; 1</td>
</tr>
<tr>
<td>IV</td>
<td>60</td>
<td>29.7</td>
<td>4.3</td>
</tr>
<tr>
<td>V</td>
<td>10</td>
<td>&lt; 1</td>
<td></td>
</tr>
<tr>
<td>V</td>
<td>60</td>
<td>11.2</td>
<td>2.8</td>
</tr>
<tr>
<td>VI</td>
<td>10</td>
<td>&lt; 1</td>
<td></td>
</tr>
<tr>
<td>VI</td>
<td>60</td>
<td>4.5</td>
<td>3.9</td>
</tr>
<tr>
<td>VII</td>
<td>10</td>
<td>&lt; 1</td>
<td></td>
</tr>
<tr>
<td>VII</td>
<td>60</td>
<td>8.1</td>
<td>2.6</td>
</tr>
<tr>
<td>VIII</td>
<td>60</td>
<td>7.6</td>
<td>5.3</td>
</tr>
<tr>
<td>IX</td>
<td>10</td>
<td>2.1</td>
<td>1.2</td>
</tr>
<tr>
<td>IX</td>
<td>60</td>
<td>17.2</td>
<td>4.5</td>
</tr>
<tr>
<td>X</td>
<td>10</td>
<td>6.4</td>
<td>1.1</td>
</tr>
<tr>
<td>X</td>
<td>60</td>
<td>30.6</td>
<td>7.8</td>
</tr>
<tr>
<td>XI</td>
<td>10</td>
<td>4.9</td>
<td>1.4</td>
</tr>
<tr>
<td>XI</td>
<td>60</td>
<td>39.7</td>
<td>14.6</td>
</tr>
</tbody>
</table>

*Not clear if they can already be called islands, since they are of the same size as a crystallite.*
Figure V-7. Island Size Distribution Using Sensitizer II

Figure V-8. Island Size Distribution Using Sensitizer III
sensitizers II and IX (of Table V-3. 60 s bath) can be seen.

Figure V-9 shows the island density vs. adsorption per unit area obtained from the adsorption studies. There is a definite trend such that higher adsorption corresponds to a higher island density.

Figures V-10 to V-13 show the photographs after one minute in the metallization bath for samples of sensitizers IV to VII respectively. (Their only difference is ageing time). The corresponding adsorption points are on Figure IV-7 (with small variations in ageing time).

Note that for sensitizer IV, the metal islands are relatively large, but rather uniform in size. The P-rich domains within the islands (lighter areas in the comb-like structure) can be distinguished. As the sensitizer ages further (sensitizer V) the islands become smaller. With sensitizers VI we obtain a bimodal island size distribution. Islands become both much smaller and larger, reflecting both the increase in sensitizer activity and the beginning of its activity decay due to colloidal aggregation (precursor of overgrown islands). With sensitizers VII clustering of many small islands is observed, although with large distance between clusters (not apparent, since only a single cluster is shown). This clustering reflects poor wetting due to space exclusion of overgrown colloids. This type of sensitization will lead to a deposit with low adherence. Note that the adsorption corresponding to this sensitizer is on the decaying
Figure V–9. Adsorption Of Sensitizer vs Island Density
Figures V–10 to V–13. TEM Photographs After One Minute In The Electroless Bath
portion, but is still relatively high, thus indicating that although the adsorption measurements in general do bear a relation to the quality of the deposit, they can sometimes be misleading if used exclusively. Our island density data has a shortcoming when dealing with clustering cases. This is so because the space between clusters is ignored (the photograph usually covers only one cluster).

The crystallite size distributions obtained from the dark field images are relatively narrow. Figure V-14 shows some of these distributions.

Table V-5 shows the average crystallite size obtained using different sensitizers. Note that in early stages of island growth, the higher the sensitizer adsorption, the smaller the crystallites. This tendency is much less pronounced for the longer deposition times, thus indicating that once the film is continuous the base layer does not play a role and the crystallite size remains practically constant. This can be seen in the dark field photographs shown in Figures V-15 to V-17. The crystallite size is affected by the variables that influence the effectiveness of the reducing system.
Figure V-14. Crystallite Size Distribution After One Minute In Electroless Bath
Crystallites Using Different Sensitizers
<table>
<thead>
<tr>
<th>Sensitizer</th>
<th>Time In Plating Bath [=] Seconds</th>
<th>Equivalent Diameter [=] nm.</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>60</td>
<td>1.53</td>
</tr>
<tr>
<td>II</td>
<td>60</td>
<td>1.41</td>
</tr>
<tr>
<td>III</td>
<td>10</td>
<td>0.84</td>
</tr>
<tr>
<td>III</td>
<td>60</td>
<td>1.56</td>
</tr>
<tr>
<td>IV</td>
<td>10</td>
<td>1.38</td>
</tr>
<tr>
<td>IV</td>
<td>60</td>
<td>1.59</td>
</tr>
<tr>
<td>V</td>
<td>10</td>
<td>1.29</td>
</tr>
<tr>
<td>V</td>
<td>60</td>
<td>1.44</td>
</tr>
<tr>
<td>VI</td>
<td>10</td>
<td>1.0</td>
</tr>
<tr>
<td>VI</td>
<td>60</td>
<td>1.5</td>
</tr>
<tr>
<td>VII</td>
<td>10</td>
<td>1.32</td>
</tr>
<tr>
<td>VII</td>
<td>60</td>
<td>1.53</td>
</tr>
<tr>
<td>VIII</td>
<td>10</td>
<td>1.27</td>
</tr>
<tr>
<td>VIII</td>
<td>60</td>
<td>1.34</td>
</tr>
<tr>
<td>IX</td>
<td>10</td>
<td>1.35</td>
</tr>
<tr>
<td>IX</td>
<td>60</td>
<td>1.49</td>
</tr>
<tr>
<td>X</td>
<td>60</td>
<td>1.69</td>
</tr>
<tr>
<td>XI</td>
<td>60</td>
<td>1.65</td>
</tr>
</tbody>
</table>

Some of our dark field exposures show crystallites with rectangular shapes. An example is shown in Figure V-18. These
rectangles are not perfectly oriented in one direction. Therefore, they are not attributed to instrument vibration. During dark field operation with electroless Ni films, the intensity is such that typical required exposures are between 20 and 180 seconds (using trial and error). It was observed that the rectangles disappear with gross underexposure. In searching for the reason for these rectangles, the beam was collimated in dark field and noted "halos" emanated from the crystallites. The very long required exposures transformed these halos into rectangles. The reason for the halos is still not clear. For image processing purposes, the crystallite equivalent diameter was assumed to be the smaller side of the rectangles.
CHAPTER VI

CONCLUSIONS AND RECOMMENDATIONS

The objective of this section is to place emphasis on the knowledge that was gained as result of the present work, and to highlight some avenues along by which this research can be continued.

A. Summary of Original Research

- The equilibrium constants for the complexation between Sn(II) and Cl⁻ in the temperature range 25 to 50 °C were determined. These constitute the first set of such constants to be reported which are useful in modeling the kinetics of the early stages of Sn(II) to Sn(IV) oxidation in dilute aqueous HCl.
- The proportionality of Sn(II) → Sn(IV) initial reaction rate in dilute aqueous HCl to [SnCl₃⁻] has been verified.
- Kinetic data were obtained for the following processes:
  + Oxidation of Sn(II) to Sn(IV) in concentrated HCl
  + Sn(IV) ion hydration and hydrolysis
  + Capture of Sn(II) by the Sn(IV) hydration products.
- A model was provided for ageing of Sn(II)-based sensitizers, that introduces for the first time the following concepts:
  + The agent responsible for high nucleation density is a surface active material whose constitutive unit is a stoichiometric Sn(II)-Sn(IV) adduct.
The surface activity bears a direct relation to chain length parallel with the case of organic chains. Cessation of surface activity is due to excessive chain growth, colloidal phase separation and continual oxidation of Sn(II) in the adduct.

- Our adsorption research, apart from its simplicity and adaptability, covered to an extent the effect of the following variables:
  + Kinetics of adsorption
  + Surface active agents as additives
  + Accelerators and inhibitors of Sn(II) oxidation
  + Mixtures of Sn(II) and Sn(IV)
  + Substrate effect.

- Overaged sensitizers were rendered useful again by breaking the colloid.

- Correlation was made between sensitizer adsorption and the subsequent metal deposit:
  + Metal islands and crystallite size distributions.
  + Metal island's nucleation density.
  + Correlation between the colloidal aggregation in the sensitizer and clustering of metal islands.

- Foundations for a systematic search of non Sn-based sensitizers.

B. Suggestions for Future Research

Only a few topics will be listed, reflecting our immediate interests only, and are by no means exhaustive;
- Preparation of organometallic molecules with reducing capabilities. This would be the first step in rendering polymers to be metallized without separate sensitization and catalyst deposition (integrated in the synthesis).
- Sizing of Sn(II)-Sn(IV) sensitizer colloids. We have reviewed extensively the literature concerning colloidal particle sizing, and so far have not found any suitable technique for these colloids.
- Determination of the mechanism of sensitization of Sn(IV).
- Study of the adsorption currents of sensitizers on a HME.
- Measurement of the contact potential at the sensitizers substrate interface.
- Measurement of the pH at the metallizing interface in the electroless bath. So far the pH is measured in the bulk of the solution. Fukunaka [80] describes an experimental technique that has the potential of measuring not only the pH at the interface, but also the concentrations of the different ions.
REFERENCES


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[79] Robinson J. W., Personal communication (June 1987).

NOMENCLATURE

E  Potential
F  Faraday constant
h  Hydrolysis constant of Sn(II)
K_e  Equilibrium constants for the complexations between Sn(II) and Cl
k  Reaction rate constant
m  Number of complexes
n  Number of electrons involved in a process
R  Ideal gas constant
r  Speed of reaction
T  Temperature

Greek Symbols

$\delta_n$  Equilibrium constants for the reactions

SnOH\textsuperscript{+} + nCl\textsuperscript{−} \rightleftharpoons Sn(OH)Cl\textsubscript{A−n}

Subscripts

n  Enumeration for successive reactions or functions.
1/2  Half wave

Miscellaneous

[X]  Molar concentration of X
APPENDIX A

NONDESTRUCTIVE QUANTITATIVE ANALYTICAL CHEMISTRY OF SN(II) IN THE PRESENCE OF SN(IV)
APPENDIX A

NONDESTRUCTIVE QUANTITATIVE ANALYTICAL CHEMISTRY OF Sn(II) IN THE PRESENCE OF Sn(IV)

This appendix reviews the limitations of analytical procedures, and focuses on the reasons polarographic method of analysis was selected.

Quantitative analysis of Sn(II) is relatively difficult because of the ease with which it oxidizes to become Sn(IV).

A comprehensive literature search showed that most techniques either do not distinguish Sn(II) from Sn(IV), showing overall Sn (e.g., atomic absorption), or are inherently destructive, oxidizing quantitatively Sn(II) to Sn(IV).

The following three families of techniques allow these determinations at a microanalytical level, and destroy a small enough fraction of the sample to be considered nondestructive:

- The method of oxidative titration with Ce(IV) or Cr_2O_7^{2-} using starch and I as indicator. It has the advantage of being simple in terms of equipment and procedure (buret, stirred beaker and inert gas masking). In actual test analysis concentration values that fluctuated up to 10% were achieved.

- Ion chromatography - was not attempted because of lack of suitable equipment. Commercial units cost upwards of $65,000.
Several electrochemical methods can perform the task: stripping voltametry, coulometry, polarography etc. Polarography was selected because it is relatively simple and a home made instrument was assembled. Also, previous experience had been gained with polarographic analysis.

The supporting electrolyte 4M NH₄Cl + 1M HCl + 0.005% gelatin (developed by Lingane [A-1]) is possibly the easiest one to prepare and work with, which allows the simultaneous determination of Sn(II) and Sn(IV).

References

APPENDIX B

VOLTAMETRY INSTRUMENTATION
APPENDIX B

VOLTAMETRY INSTRUMENTATION

This appendix describes the home designed and assembled instrument used for analytical purposes. A technique that emulates a hanging drop electrode (HDE) with a regular dropping Hg electrode (DME) called "pseudo single drop voltametry" is also presented.

A. Instrument Specifications
- Set a potential between -3 and 3V against a reference potential in 255 steps of 2.34 mV each.
- Measure a current between -300 and +300 nA in steps of 2.34 nA, and ranges of 10, 100 and 1000 multiples.
- Obtain I(V,t). It has been tested at frequencies up to 1 KHz with simple waveforms (ramps and square waves). Maximum operating frequency depends on the actual nature of the waveform.
- Fan out up to 30 mW power.

B. Configuration
The basic instrument configuration is shown in Figure B-1.

The computer used in this project is a TRS-80 64K colour computer II.

The parallel expansion connector allows ease of access for wiring purposes.
From among the 32 memory addresses to which the parallel expansion port connector allows access, the decoder selects 16. In this instrument only two of them are used: FF40 and FF41.

The instrument applies a waveform by writing it in discrete steps to address FF40. In addition, one write and one read signal to FF41 are used in the A/D conversions involved in the current measurements (One pair per each D/A cycle constituting the A/D conversion.). The three previous read/write operations are triggered with select signals generated using proper logical gates.

After the generation of the corresponding trigger signals, the computer either outputs or is ready to receive data through the bus for a short time, which is not long enough for the I/O equipment to respond. Hence data is held by latching.

One D/A unit is responsible for the potential application to the Hg pool. The other D/A unit together with the comparator constitute an A/D converter used for the current measurements as follows: For each conversion, initially the most significant bit of the data byte is set all others reset. The byte is written and a signal (MSB of data byte) is read back in which the current is either higher or lower; in the latter case the bit previously set is reset. The next significant bit is set and a similar test performed again until all eight bits are tested and either set or reset.
The voltage application and current measurement unit has as its objective the application of potential and the measuring of current simultaneously using a single wire. The circuit is shown in Figure B-2. Mode of operation: The applied potential $E_1$, comes from the D/A converter. Since both inputs to an op-amp are at the same potential, $E_1$ is applied to the Hg electrode and current $I$ is generated.

$$E_2 = E_1 + IR$$

The second op-amp subtracts $E_1$ so:

$$E_3 = E_2 - E_1 = IR$$

Hence each current is related to a voltage from $-3$ to $+3V$ for $E$ of any range. Four ranges are provided, spanning current steps from $2.34$ nA to $2.34$ mA.

The comparator is a full-swing op-amp which is clamped with a diode because the TTL logic receiving the signal can be damaged by negative voltages.

Table B-1 lists the specific integrated circuits used for each building block, note that these are not necessarily the most adequate ones, they were selected simply because they were immediately available.

C. **Pseudo Single Drop Voltametry**

In pseudo single drop voltametry the voltage sweep and current measurement take place during the last one percentile of the drops life time. The surface area is considered practically constant, thus emulating a HDE. (higher
Figure B-2. Voltage Application And Current Measurement Circuit
resolution, faster potential sweep rates than DME and no current oscillations).

**TABLE B-1**

**Instrument Main Components**

<table>
<thead>
<tr>
<th>Building Block</th>
<th>Integrated Circuit</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Decoder</td>
<td>SN74154</td>
<td></td>
</tr>
<tr>
<td>Generation of</td>
<td>DM7423</td>
<td>The signals could be generated without 7402N connections. These however were found unreliable.</td>
</tr>
<tr>
<td>of select signals</td>
<td>7402N</td>
<td></td>
</tr>
<tr>
<td></td>
<td>7404</td>
<td></td>
</tr>
<tr>
<td>Latching</td>
<td>SN7475</td>
<td>only one three state bit is needed. The SN74LS373 provides eight.</td>
</tr>
<tr>
<td></td>
<td>Sn74LS3737</td>
<td></td>
</tr>
<tr>
<td>Reference power supply</td>
<td>CA3140</td>
<td></td>
</tr>
<tr>
<td>Voltage application and</td>
<td>MC3400</td>
<td></td>
</tr>
<tr>
<td>current measurement</td>
<td></td>
<td></td>
</tr>
<tr>
<td>D/A units</td>
<td>MC1408-8</td>
<td></td>
</tr>
<tr>
<td>Comparator</td>
<td>MC3400</td>
<td></td>
</tr>
</tbody>
</table>

1. **Adaptation to DC Polarography**

The implementation of the present technique to DC polarography requires the setting of four parameters:
potential range, instrument current range (by hardware), sweep rate and potential at which the Hg drops are to be timed.

The following four modules constitute the implementation:

- Current measurement: It is achieved by successive digital to analog conversions. Delays are incorporated such that each current measurement should take equal amounts of time.

- Detection of a new drop: Once the Hg pool is set at a specified potential, current measurements are performed successively for as long as the current increases. The currents sudden decrease is an indication of a new drop.

- Drop life time measurement: First a new drop is detected. Then the same procedure as for the detection of a new drop is followed, this time counting the number of current measurements. Several drops are timed to ensure reproducibility.*

- Potential sweep and current measurement: Figure B-3 shows the flowchart for an arbitrary waveform.

2. Source Code

The previous instrument description should suffice for anyone interested in writing a source code for regular DC polarography. But the pseudo single drop implementation of DC polarography requires specific knowledge of the computer CPU, ...

*In the source code given the number of drops timed was fixed (5) but it can be changed.
Figure B–3. Pseudo Single Drop Voltametry For An Arbitrary Waveform
hence the assembly language subroutines that control the operation are provided.

To interact with the subroutines, the main program must follow this procedure:

- Load BASE0 the address where the first drop life time is stored (Next addresses contain lives of subsequent drops. Lives are stored as number of current measuring cycles).
- Load SPEPOT the potential meanwhile waiting for a new drop.
- Call ENTRY1
- Decide if drops lives are stable
- Load the following variables:
  - BASE1 Address where current corresponding to lowest potential is stored (next address corresponds to next potential step).
  - LOWLIM Lowest potential to be swept (0 --- > -3V, 255 --- > +3V)
  - HIGHLM Highest potential to be swept
  - DELAY2 Two bytes long integer that must be calculated according to the following formula:
    Time for one potential sweep step [=] seconds =
    = (9 * DELAY2 + 6)/895000 + 5.33E-05
- Call ENTRY2

* SUBROUTINE ENTRY1
* Purpose: To measure the drop life for a certain number of drops (set to 5
but it can be changed at will)

Global Variables:

BASEO.- Address where first drop life time is stored

CURCON.- Most recent current

CURRE.- Previous current

TICOUN.- Drop Life (in current measurement cycles.

Local Variables:

ADDREO.- Address where drop life is stored

DISPO.- Displacement to calculate ADDREO

Subroutines Called: INITI, ATOD

ENTRY JSR INITI Detect new drop
LDD #$0
STD TICOUN Initialize drop life to zero
LDD #$5 Five drops to be measured (change to any other number)

STD DISPO Initialize counter

LOOP0 JSR ATOD
LDA CURCON Obtain and store first current
STA CURRE

LOOP1 LDD #$1
ADDD TICOUN Increment the drop life timer by one
STD TICOUN
JSR ATOD
LDA CURCON Obtain next current
ANDCC $FE Set carry bit to zero
SBA CURRE If previous current < previous one set carry bit

LDA CURCON
STA CURRE Save new current
BHS LOOP1 If current continues increasing repeat the cycle

LDD BASEO Calculate address to store drop life
ADDD DISPO
STD ADDREO
LDD TICOUN
STD [ADDREO] Store drop life
DEC DISPO2 Two byte address so decrement twice
DEC DISPO2
BNE LOOP0 Repeat the procedure until the required number of drops have been timed

RTS Return

* SUBROUTINE ENTRY2
* Purpose:
* a) Detect new drop
* b) Wait until 99% of drop life
* c) Set voltage, measure current and record
them, with as many drops as necessary.

Global Variables:

BASE1. - Address where current corresponding to lowest potential is stored.

DELAY1.- Auxiliary to wait until 99% of drop life

DELAY2.- Auxiliary to set frequency of sweep

DROP CY.- Current measurements per drop

HIGHLM.- Highest potential to be swept

LOWLM.- Initially contains lowest potential to be swept increases until reaches highLM.

Local Variables:

ADDR1.- Address where current is stored

DISP1.- Displacement to calculate ADDR1

DISP12.- Low order byte of DISP1

Subroutines Called: INITI, ATOD, TIMEDN

ENTRY2 JSR INITI Detect new drop

JSR TIMEDN Delay large period of time

LDD DELAY1 Wait until 99% of drop life
LOOP2 NOP

SUBD #$1
BNE LOOP2
LDB DROP CY

INCB Initialize number of measurements per drop

* LOOP3 DECB Can we get another cycle with this drop?

* BEQ ENTRY2 or lets get a new one
LDA LOWLIM
STA $FF40 Apply potential
JSR ATOD Obtain Current
LDD BASE1 Evaluate the address where current is
ADDD DISP1 to be stored
STD ADDR1
LDA CURCON
STA [ADDR1] Store current
INC DISP12 Two byte address so increment
INC DISP12 displacement by two
LDD DELAY2 Wait so sweep will be at specified frequency

LOOP4 NOP

SUBD #$1
BNE LOOP4
INC LOWLIM Obtain new potential
LDA HIGHLIM
SUBA LOWLIM Check if potential sweep is complete
INCA

BEQ LOOP3

RTS   Return

*  
* SUBROUTINE INITI
*  
* Purpose:
*  
a) Set drop at specified potential  
b) Do A/D until current falls (Indication of  
   new drop)
*  
* Global Variables:
*  
*     CURCON.- Most recent current
*     CURRE.- Previous Current
*     SPEPOT.- Potential meanwhile waiting  
   for new drop.
*  
* Subroutines Called: ATOD

INITI CLRA

STA  CURRE  Initialize current to zero
LDA  SPEPOT  Set Drop at specified potential
STA  $FF40

LOOP5 JSR  ATOD  Do A/D conversion
LDA  CURCON  Get Current
ANDCC $FE  Set carry bit to zero
SUBA  CURRE  If new current < previous one
       set carry bit
LDA  CURCON
STA  CURRE  Save new current
BHS LOOP5 If current continues increasing, repeat
RTS Return

* SUBROUTINE ATOD
* Purpose: Carry analog to digital conversion
* Global Variables:
* CURCON - Current
* Local Variables:
* CICLEN - Number of bits to be tested before finishing A/D conversion (initially 8).
* Duration = 477 machine cycles = 0.53296 milisec.

ATOD CLRA
STA CURCON Initialize current to zero
LDB #$8 Initialize number of bits
STB CICLEN to be tested (8)
LDA #$80 Set MSB
LOOP6 STA $FF40, Apply potential
SUBA CURCON Leave in register A the bit currently being tested
LDB $FF41 MSB of FF41 = (1 --> current higher)
TSTB
BPL CURMIN Branch if current is lower
TFR A,B
Add the bit under test to the
previously
*
ADD B CURCON
set byte
STB CURCON
BRA AVOID No time killing required
CURMIN LDB #$2
KILL BRN CURMIN This section is to kill time so each
DEC B conversion will take the same amount
BNE KILL of time
AVOID RORA Move bit to be tested to the right one
* position
ANDA $7F Set MSB to zero (in case carry was not
* zero before the shift)
* ADDA CURCON Set new current to be tested
DEC CICLEN Did we check all 8 bits? if not repeat
BNE LOOP6 the cycle again
RTS return

* SUBROUTINE TIMEDN
* Purpose: To delay large periods of time
* Global Variable:
* DELAYO
* Time delay in seconds = 0.659 * DELAYO
TIMEDN LDP #$FFFF
KTIME NOP
SUBD #$1
BNE KTIME
3. **Instrument and Technique Performance**

Figure B-4 shows pseudo single drop polarography sweeps (at 20 V/Min.) for Sn(II)/Sn(IV) solutions. Figure B-5 shows the linearity of the diffusion currents with concentration for the waves of Figure B-4.
Figure B-4. Pseudo Single Drop Polarographic Waves
Figure B-5. Diffusion Currents vs Concentration
APPENDIX C

GRAPHICAL REPRESENTATION OF Sn(II)-Cl- EQUILIBRIA
APPENDIX C

GRAPHICAL REPRESENTATION OF Sn(II)–Cl− EQUILIBRIA

Since almost all Sn(II)-based sensitizers contain [Cl−] from 0.05 to 1.0M. It was considered useful to represent graphically the equilibria of Sn(II) species in this range.

Figures C-1 to C-6 show graphically the equilibria of Sn(II) species for [Cl−] between 0.05 and 1.0M, for the temperature range 25 to 50°C in steps of 5°C.
Figure C-1 Sn(II) Species Equilibria at 25°C
Figure C-2 Sn(II) Species Equilibria at 30 °C
Figure C-3 Sn(II) Species Equilibria at 35 °C
Figure C–4 Sn(II) Species Equilibria at 40°C
Figure C-5 Sn(II) Species Equilibria at 45°C
Figure C-6 Sn(II) Species Equilibria at 50°C
APPENDIX D

SAMPLE PREPARATION FOR TEM
APPENDIX D
SAMPLE PREPARATION FOR TEM

The most difficult and frustrating part of the TEM work was the mastering of a technique for preparing suitable samples.

Self-supporting electron-transparent films (at 100KV) can be produced from some materials, such as graphite and Al, due to one of the following properties:
- Constitutive atoms are of a low atomic number.
- Material which is crystalline.

Electroless Ni deposits range from polycrystalline to practically completely amorphous, and Ni has a high atomic number. Hence no continuous electron-transparent films are produced. Therefore, electroless Ni deposits are studied while supported on another film. The deposit is observed during various stages of growth until it forms a continuum.

The ideal supporting film would have the following properties:
- One hundred percent electron transparency (no beam attenuation).
- Zero thickness (very thin compared to deposit on top)- two reasons for zero thickness: first, as in the previous point, electron attenuation is minimal; second, surface imperfections or waviness do not cause depth of field limitations when focussing.
Complete amorphism, so no structure will be superimposed on a diffraction pattern.

- Electrical conductivity to avoid charging effects.
- Ability to withstand temperatures up to 250 °C without deteriorating (The electron beam can heat the sample considerably unless a cold stage is used).
- Strength to tolerate being handled in the different baths of the metal deposition process.
- Resistance to all the pH scale.
- Appropriateness as a representative substrate onto which electroless Ni is deposited in practice.
- Ease of preparation.

Searching for the best combination of the previous properties, past researchers have used collodion, cellulose acetate, formvar, butvar and graphite replication on glass.

In the process of developing our technique, other polymers were tried without much success. Formvar solutions in ethylene dichloride seemed the best compromise.

The literature describes various techniques (eg. [D-1] to [D-3]). The following steps summarize most of them:

- Preparing a solution of between 0.1 and 0.4% by weight formvar in either ethylene dichloride or dioxane.
- Coating a precleaned glass slide:
  + By passing the solution through a vertical pipe with the slide inside.
+ By dipping a slide in the beaker of the solution, removing it, and letting it dry.
+ By first immersing the slide in the solution, removing it, and then letting it drain in an atmosphere saturated with the solvent for half an hour before drying.

- Electroless deposition with the formvar film covering the glass.
- Flotation of the film from the glass by scraping the edges and/or cutting a square of film with a knife and immersing it in water. There are different styles of immersing as well:
  + Lowering the slide into water at a slight angle.
  + Plunging the slide vertically into water and taking it out slowly, so that the film floats off on the water.
- Placing the grids on top of the film which is still floating on water, and trapping it with another slide such that the grid stays between the glass and the film. Alternatively, the film can be trapped with a piece of metal with holes which hold the grids.

Various and sometimes conflicting suggestions are made of ways to facilitate film separation from the glass:
- Smearing a drop of liquid soap, such as "topol", on the slide.
- Smearing oil on the slide.
• Keeping the solution grease-free, since traces of grease prevent separation from occurring.

• Taking particular care in cleaning the slides and handling all materials with tweezers.

The biggest problem encountered is how to float the film. A relatively thick film e. g. 400 nm is easy to float, but no electrons go through it. As the film is made thinner, it becomes more difficult to float. The higher the magnification desired, the thinner the supporting film has to be. Hence, what might be a "good" sample at 20,000 X, might be useless at 100,000 X.

The formvar thickness for a suitable sample at 100,000 X is approximately 40 nm, and the average thickness of the metal film on the onset of continuity is an order of magnitude smaller, so this is far from the ideal.

Following carefully the techniques described in the literature, at best 5% success was achieved when it came to floating the films.

Clearly there are several unexplored parameters which may cause irreproducibility, the main ones being:

• Characterization of the formvar used.

• Final use of the films (work magnification).

• Characterization of the surface of the glass slides. We found that the slides of some boxes are much easier to float than the ones from other boxes (even when both boxes came from the same manufacturer).
For the benefit of future researchers, an extensive description of the technique which we developed empirically is shown in Figures D-1 to D-3.

Precleaned slides out from the box are wiped with paper before being used, but note, that the edges and the frosted section can be touched with the fingers.

References


40 mm diameter
18 cm long before
the reduction

glass slide
(not to scale)

wire hanger

formyvar
% weight

<table>
<thead>
<tr>
<th>% weight</th>
<th>draining time (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.4</td>
<td>60 – 100</td>
</tr>
<tr>
<td>0.2</td>
<td>20 – 40</td>
</tr>
<tr>
<td>0.1</td>
<td>10 – 15</td>
</tr>
</tbody>
</table>

reduction
4.5 cm long
7 mm diameter

pinch clamp
(for fill up)

rubber hose
3 cm

Tip from an injection needle. Diameter varies
(to control flow rate)

to bottle

Figure D-1
Apparatus Used For Casting Films
Figure D–2. Film Flotation
Figure D–3. Grid Mounting
APPENDIX E

IMAGE PROCESSING
APPENDIX E

IMAGE PROCESSING

In order to appreciate the difficulties in image processing, a description of the problems encountered in the use of traditional techniques is given.

A. History

This type of work requires processing images and diffraction patterns. The latter are relatively straightforward to process: photodensitometers with moving trains and film holders that allow rotation have performed an excellent job for many years. In case of images when it came to sizing, digitalizing tablets were used, but they have the following limitations:

- Very often the tip of the pen used in conjunction with the tablet is of the same order of magnitude as the features to be sized. In this case, enlarged positive prints are required. Besides the optical error, the expense involved is considerable. In the system we will describe, the image is usually expanded, but is only one step from the negative to the digital file, and no prints are required.

- When the number of features to size and/or count lies in the hundreds and up, the tediousness involved causes many human errors.

- The borders of the islands can be distinguished only before they fuse. This results from the limitations of the
average human brain which can distinguish as many as about sixteen gray levels between "white" and "black". They are condensed in a very narrow band as illustrated in figure E-1.

B. Experimental

A schematic of the digitalizing instrumentation is shown in Figure E-2.

From each negative several digitalized files were made. The digitalizing requires two precautions:

- The resolution of the border of the islands is dependant on the illumination; the more intense it is the larger dispersion on the brightness values is obtained. The fluorescent lamp the holder comes with, has to be replaced with a collimated point source (spot light), which also has the added advantage of giving a more uniform illumination (the shape of the lamp does not render uniform illumination, the diffuser is intended to make it more uniform. The film holder has plenty of room for improvement).

- The plexiglass, spot light and camera lens have to be perfectly clean, any dust particle will be taken as a feature on the image.

Sizing of objects with well defined borders is encountered in many fields of science (e.g. differentiating bacteria), therefore algorithms are well established. Files
Top view of model film. Metal islands represented as half spheres.

Cross sectional view of some of the islands and the brightness they produce on a negative:

Human brain outside the band: above everything is "white" below everything is "black"

Figure E-1. Human Brain Image Processing
Figure E-2. Image Digitalizing Instrumentation
were processed using the source code provided by Schildt [E-1] (with minor modifications).

The system performance was verified twice:

- Two frame grabbers for digitalizing were used. All the work was done using the one described by Ciarcia [E-2]. Selected areas of some negatives were also digitalized using a VIP grabber. Although the brightness values of both sets of files were not identical, they were proportional to each other in more than 98% of the pixels.

- The distribution of one negative with large islands was also obtained by using a digitalizing tablet. The average of both distributions were within 10% of each other.

References


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