THE UNIVERSITY OF MANITOBA

A STUDY OF THE COMPLEX FORMED BETWEEN PLATINUM AND TIN(II) CHLORIDE IN AQUEOUS SOLUTION

by

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A dissertation submitted to the Faculty of Graduate Studies of
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I. Abstract

This work studied the complexes formed between platinum and tin II chloride in an aqueous medium.

The electronic spectrum of $PtCl_4^{-2}$ showed that in preparing the platinum samples for complexation, treatment with perchloric acid in a chloride, sulphuric acid medium caused oxidation to $PtCl_6^{-2}$.

Simultaneous polarographic determination of tin(II) chloride and amperometric titration of $PtCl_6^{-2}$ with tin(II) chloride in a chloride, sulphuric acid, perchloric acid medium showed that tin(II) chloride reduces Pt(IV) to Pt(II) and forms a 1/1 complex in tin and platinum(II).

Spectrophotometric studies were done which suggested the formation of at least two other platinum(II) - tin(II) chloride complexes in equilibrium with one another involving tin to platinum ratios of greater than 1/1.

A Study of the Complex Formed Between Platinum and Tin II Chloride in Aqueous Solution

II. Introduction

On mixing a solution of platinum in an oxidation state of II or IV with a solution of tin(II) chloride a bright red or yellow solution is known to form. These coloured solutions permit a very specific, highly sensitive spectrophotometric determination for platinum at concentrations as low as 0.08 ppm.[1] The specificity and relative simplicity of this procedure as compared to gravimetric methods make the spectrophotometric determination of platinum a very valuable analytical tool. Kane[2] first observed these coloured solutions in 1835; however, no agreement has yet been reached as to the stoichiometry of the complexes formed or the oxidation state of the platinum in the complexes.

Ayers and Meyer[3,4] made the first significant step in attempting to understand the complex. They prepared their solutions using a tin to platinum ratio of 4000/1 and observed absorption maxima in the electronic spectrum at 403 and 310 nm. They proposed a complex with platinum having an oxidation state of zero. Using platinum(IV), Ayers and Meyer employed a method of continuous variations and claimed evidence for complexes involving tin to platinum ratios of 2/1, 3/1, and 5/1. Ayers and Meyer found that more than one complex was formed and that one formed quickly and the others more slowly. They showed that the complex could be extracted from aqueous solutions by alcohols and ketones and could be precipitated from aqueous solution by phenylarsonic acid. Ayers and Meyer claimed this ability to be precipitated by phenylarsonic acid showed that the complex was a tetrapositive cation; however, later work[10] did not agree with this and the complex is considered to be anionic.

Milner and Shipman[5] indicated that the complex was most stable in a 0.3N hydrochloric acid solution with a molar ratio of tin to platinum of 400/1. They also suggested a mixed complex involving platinum with tin(II) and tin(IV) because they found a higher colour intensity when tin(IV) was present.

No real agreement could be reached on optimum conditions for colour development and Smith[6] used a tin to platinum ratio of 10,000/1.

In Ayers and Meyer's[3,4] work they identified absorption maxima at 403 and 310 nm. However, the absorption of the reagent blank made accurate measurement of the absorption maximum at 310 nm impossible. Berman and Goodhue[1] were able to make use of this absorption maximum by using a sulphuric acid, perchloric acid medium. They found that this medium stabilized the complex and caused a hypsochromic shift of the tin absorption, thus making the absorption of the complex at 310 nm observable. Berman and Goodhue's method gave five times the sensitivity of previous methods in hydrochloric acid and they found Beer's Law to be obeyed from 0.08 ppm to 6.0 ppm of platinum. They still used however a large excess of tin(II) chloride for colour development.

Bard,[7] using coulometric titration with electrogenerated tin(II) suggested that tin(II) can only reduce platinum(IV) to platinum(II), yet he conceded that a chloride medium and a 50-300 fold excess of tin(II) would favor reduction of platinum to an oxidation state of zero. He also stated that a tin to platinum ratio of 5/1 does not cause a reduction of platinum(II) to platinum in a zero oxidation state and that this reduction of platinum(II) by tin(II) is a slow reaction under any conditions. More recent work[8,9] suggests that the reduction of platinum to a zero valent state occurs rapidly and completely in solutions containing tin(II) to platinum ratios of less than 5/1.

Using adsorption paper chromotography Lederer and Shukla[10] showed that the platinum-tin complex is anionic, whereas Ayers and Meyer[3,4] had suggested it to be cationic. They[10] also suggested that trichlorostannite ligands ($SnCl_3^-$) were co-ordinated to the platinum and that a zero valent platinum was highly unlikely.

Davies _et al_[11] confirmed that the complex was anionic through ion exchange study and gave further weight to the suggestion of trichlorostannite ligand in a 3.0N hydrochloric acid medium. Davies et al precipitated tetraalkylammonium salts of what analysed to be $[Pt(SnCl_3)_2Cl_2]^{-2}$ and stated that this could best be considered a complex of tin(II) and platinum(II). They also isolated a neutral $[(C_6H_5)_3P]_2PtClSnCl_3$ complex salt, but these results, although somewhat illuminating do not lead to any definite conclusions concerning the state of the platinum-tin complex in solution.

Cramer et al[12] found that the complex formed between platinum and tin(II) chloride is an effective hydrogenation catalyst, yet a requirement was that the tin(II) to platinum(IV) ratio be greater than 5/1 for maximum hydrogenation rates. They isolated two other substances which further complicate the system.

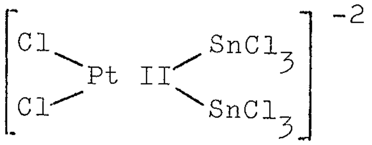
$[(C_6H_5)_3PCH_3]_3Pt(SnCl_3)_5$ (red crystalline) and

$[(C_6H_5)_3PCH_3]_2PtCl_2(SnCl_3)_2$ (yellow crystalline)

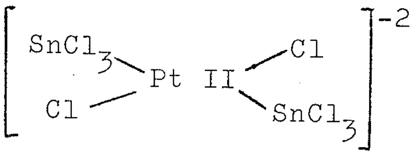
In further work Cramer et al[13] showed that the $[Pt(SnCl_3)_5]^{-3}$ anion is trigonal bypyramidal by using X-ray diffraction. They also reported having prepared salts of: $[HPt(SnCl_3)_4]^{-3}$ and $[HPt(SnCl_3)_2((C_2H_5)_3P)_2]^{-1}$.

Yamamoto et al[14] using electrophoresis and oxidation tests, stated that complexes of platinum(II) and tin(II) are formed with tin to platinum ratios of 1/2, 1/1, 3/1, and 5/1 but that these anionic complexes tend to decompose to red colloidal platinum and tin(IV) in an inert atmosphere.

Young, Gillard and Wilkinson[15] published a most comprehensive paper on the tin(II) chloride complexes of ruthenium, rhodium, iridium and platinum in which they propose the possibility of the existence of cis and trans isomers of the anionic species



and



In an ethanol solution of sodium chloroplatinite, addition of anhydrous stannous chloride to give a tin to platinum ratio of 2/1 gave an orange-red solution which in fifteen minutes became an orange-yellow solution. Immediate precipitation of the orange-red solution with tetramethylammonium chloride gave a red salt whereas precipitation of the orange-yellow solution gave a yellow salt. They found that this reaction also occurred in 3.0N hydrochloric acid solution. Analyses of the red and yellow salts were the same but their X-ray powder patterns were different. The red "isomer" was found to be predominant in ethanol and hydrochloric acid solutions of high tin to platinum ratios and predominated initially in solutions with tin to platinum ratios of 2/1. At tin to platinum ratios higher than 8/1 Young _et al_[15] state that the red isomer is the only form present at room temperature.

The authors[15] associated the red isomer with absorption maxima in the electronic spectrum at 401, 310 and 254 nm and the yellow isomer with absorption maxima at 310, 278 and 254 nm.

In ethanol solutions with tin to platinum ratios of 5/1 Young _et al_ prepared the yellow tetramethylammonium chloride salt at -70° C. On warming they observed the crystals turn red.

The yellow isomer was assumed to be the cis isomer which would be more thermodynamically stable due to $d\pi - d\pi$ bonding. The yellow isomer had bands at lower wavelengths in its electronic spectrum than the red isomer, which would indicate greater stability. The yellow isomer was more soluble in polar solvents such as hydrochloric acid as would be expected for the cis isomer.

The authors[15] proposed a stepwise complex formation and the strong trans effect of the trichlorostannite ligand as reported by Lindsay et al[16] would favor the initial formation of the red trans isomer. Excess trichlorostannite ligand would allow only the trans isomer by suppressing the dissociation through which Young et al[15] suggest the cis isomer is formed.

$$SnCl_2 + Cl^- \longrightarrow SnCl_3^-$$

$$PtCl_4^{-2} + SnCl_3^- \longrightarrow PtCl_3(SnCl_3)^{-2}$$

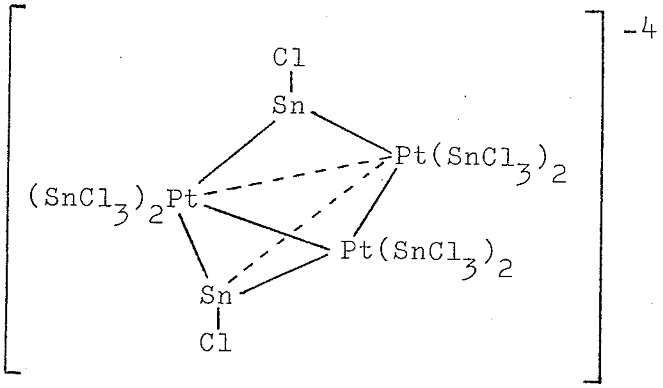
$$PtCl_3(SnCl_3)^{-2} + SnCl_3^- \rightleftharpoons \text{trans - } PtCl_2(SnCl_3)_2^{-2} + Cl^-$$

$$\text{trans - } PtCl_2(SnCl_3)_2^{-2} \rightleftharpoons \text{cis - } PtCl_2(SnCl_3)_2^{-2}$$

Although no evidence for quinquecoordinated ions such as $[Pt(SnCl_3)_5]^{-3}$ as reported by Cramer[13] was obtained, Young et al agreed that they exist and are stabilized in crystals by large cations.

Preparing the complex using platinum(IV) and tin(II) chloride, Khattak and Magee[17] showed that the complex was extracted from aqueous solution by high molecular weight amines. They suggested that the extractions caused little or no structural change in the complex as the electronic spectrum between 350 and 600 nm showed no change but there was a five-fold increase in sensitivity over the same amount of the platinum-tin complex in an aqueous phase.

Lindsay _et al_[18] further complicated the problem of understanding the platinum-tin(II) chloride complex when in acetone solution they found evidence for an anion $[Pt_3Sn_8Cl_{20}]^{-4}$.



This anion apparently contains platinum in a zero valent state.

All of the studies done, show that the complex formed between platinum and tin(II) chloride involves a very complicated system in which there is evidence for zero valent platinum, platinum(II), tin(II), tin(IV), and the $SnCl_3^-$ ligand in which the tin is considered to be divalent as well as tetravalent[19] as in

$SnCl_4$. The complexity of the system has led most workers to try to precipitate something from the complex system, analyse the precipitate and in this way determine the state of the complex. This can sometimes be misleading however, since it would appear that $[Pt(SnCl_3)_5]^{-3}$ only exists when stabilized by large cations and this anion is not a species which exists in an aqueous medium without large cations. It was the purpose of this work to attempt to study the complex as it was forming and after it had formed in the aqueous medium in which it was prepared. Spectrophotometric and polarographic studies were made on the complex as these methods were available and allowed study of the system with a minimum of interference with the complex system. The major difficulty in this type of study was to control enough of the variables in this very complex system so that a valid study could be made on any one aspect of the complex. More often the complexity of the system determined what could be studied and accomplished.

III. Apparatus and Reagents

The following materials and equipment were used during the course of this work.

Unicam SP500 series 2 Ultraviolet and Visible Spectrophotometer

Perkin and Elmer Model 450 Ultraviolet, Visible and Near Infrared Spectrophotometer

Sargent Polarograph Model FS

Polarographic Cell (fig 10)

Unicam SP90 Atomic Absorption Spectrophotometer

Thermolyne - Type 1300 Furnace

Sartorius Microbalance Model MPR5

Corning PC100 Hot Plate

Platinum Wire for platinum(IV) solutions (99.9% pure - Johnson Matthey and Mallory Chemicals Ltd.)

$PtCl_2$ for platinum(II) solutions (Goldsmith Chemical and Metal Corporation)

Reagent grade chemicals and doubly distilled water were used throughout this work and all volumetric equipment was calibrated prior to use.

IV. Preparation and Standardization of Solutions

A. Preparation of Stock Platinum Solutions

Platinum (IV)

0.950 gm of platinum wire were dissolved in aqua regia, evaporated to near dryness, taken up in 20 ml of concentrated hydrochloric acid and evaporated to near dryness. The hydrochloric acid treatment was repeated three times and after the final evaporation 10 ml of concentrated hydrochloric acid and 5 mg of potassium chloride were added. The solution was transferred to a 1000 ml flask and diluted to the mark with water.

Platinum (II)

1.364 gm of platinum dichloride were dissolved in 10 ml of concentrated hydrochloric acid. Five milligrams of potassium chloride were added and the solution was transferred to a 1000 ml flask and diluted to the mark with water.

For the purposes of this work more dilute solutions of platinum were required. Dilute solutions of platinum (IV) and platinum (II) were prepared by transferring 30.04 ml of the stock platinum solutions to 1000 ml volumetric flasks. Five milligrams of potassium chloride and 10 ml of concentrated hydrochloric acid were added and the solutions were made to the mark with water.

B. Preparation and Standardization of Tin(II) Chloride Solutions

For this work a tin chloride solution was required which had a known concentration and which had, ideally, all of the tin in an oxidation state of two.

Iodometric titration[29] was chosen for the tin(II) determination. The iodine solution was standardized using arsenious oxide.

Experimental

Arsenious oxide was dried to constant weight in a dessicator over sulphuric acid[29] before 1.978 gm were weighed out and transferred to a beaker. To this 2.0 gm of sodium carbonate and 45.0 ml of water were added and the mixture was heated until the solids dissolved. The solution was transferred quantitatively to a 500 ml volumetric flask. To the solution 10.0 ml of concentrated hydrochloric acid and 10.0 gm of sodium bicarbonate were added and the solution was diluted to the mark with water. The iodine solution was titrated with the arsenious oxide solution and standardized as $(0.990 \pm 0.002) \times 10^{-2}M$ according to the equation:

$$As_2O_3 + 2I_2 + 5H_2O \rightleftarrows 2H_3AsO_4 + 4I^- + 4H^+$$

In preliminary trials tin(II) chloride solutions were prepared using $SnCl_2 \cdot 2H_2O$. These solutions, which were 1.5M in hydrochloric acid, were prepared under nitrogen using deaerated water. The tin(II) concentration of solutions prepared in this manner were determined iodometrically and found to be as much as 30% lower than expected. Attempts to analyze for total tin content using oxidation followed by hydrogen reduction and atomic absorption studies failed to provide answers to the unexpected results and the method was discarded. A second method of preparation of tin(II) chloride solutions was investigated.

Approximately 0.30 gm of mossy tin were dissolved in 50 ml of concentrated hydrochloric acid under a nitrogen atmosphere and the resulting solution transferred quantitatively to a 1000 ml volumetric flask containing 500 ml of deaerated water. Water and hydrochloric acid were added to yield an aqueous solution 1.5M in hydrochloric acid. The tin(II) concentration was determined by iodometric titration.

Results

As can be seen from table 1 the tin(II) chloride solutions prepared by the above method were found to be approximately 2% lower than the expected tin(II) concentrations based on the weight of mossy tin added. This slight deviation was attributed to minor oxidation of the tin(II) to tin(IV). The tin(II) concentration proved to be stable within 1 - 2% over a three hour period, however, even under an inert atmosphere the tin(II) concentration dropped by about 10% after 24 hours. This finding conflicts with the stability of tin(II) solutions as reported by H. Basinska and W. Rychcik[20] despite similar storage conditions. The method of preparation, however, was quite different and this might account for the disagreement in reported stability.

Since the solutions were not stable over 24 hours the tin(II) chloride solutions for this work were prepared daily. The solutions were prepared at such concentrations so as to give as nearly as possible whole number molar ratios between tin(II) and platinum when convenient additions of tin(II) were made to the platinum solutions.

Table I - PREPARATION AND STANDARDIZATION OF TIN II CHLORIDE SOLUTIONS

WEIGHT OF MOSSY TIN	[SnII] CALCULATED	[SnII] FOUND	PERCENT DIFFERENCE
0.314 ± 0.001 gm	2.65×10^{-3}M	2.56×10^{-3}M	3.4
0.300 ± 0.001 gm	2.53×10^{-3}M	2.50×10^{-3}M	1.2
0.272 ± 0.001 gm	2.28×10^{-3}M	2.23×10^{-3}M	2.2

C. Standardization of Platinum Solutions

The gravimetric determination of platinum using thiophenol precipitation as reported by Currah *et al*[21] and Beamish[22] was chosen as the method of standardization.

Experimental

Five drops of pure thiophenol were added to 20.0 ml of stock platinum(IV) solution. The mixture was boiled for two hours and the resulting precipitate digested on a steam bath for twenty-four hours after which time the supernatant liquid was found to be clear. The precipitate was filtered using Whatman #44 7 cm ashless paper and the precipitate was placed in a crucible which had previously been dried to constant weight. The crucibles containing the filter paper and precipitate were placed in a muffle furnace. The samples and a blank which had been prepared simultaneously were ignited at 400° C for three hours and then at 800° C for thirty minutes in order to weigh as the metal.

The deviation between replicate samples was as high as 10% and on the average the results were lower than expected by 8%.

The above standardization procedure was repeated using fresh thiophenol for the platinum(IV) and platinum(II) solutions.

Results

The first attempt at standardization produced a yellow-orange precipitate, whereas the trials with the fresh thiophenol produced a yellow-green precipitate. The deviation between replicate samples using the fresh thiophenol was 0.3%. When results from replicate samples were averaged and the platinum concentration calculated, the concentration of platinum was found to be 0.2% higher than expected based on the preparation of the stock solution. The concentrations of the stock and diluted stock platinum(IV) and platinum(II) solutions are shown in table (II).

Discussion

Beamish[22] reported that the yellow-orange precipitate observed in the first standardization attempt is associated with the product of platinum and partly oxidized thiophenol and that precipitation is incomplete. The yellow-green precipitate of the second attempt $(C_6H_5S)_2Pt$ was the desired product.

Beamish also reported that a result 0.2% high is a regular occurrence in this method, but since this result was within the deviation between replicate samples for this work, it was not considered to be a problem.

In considering this reported regular error however, the reason may lie in the inflexibility of the suggested method. Even after subtraction of the mass of a blank to account for any residue from the ashless filter paper it appears that the presence of the platinum causes an unexpected increase in mass. For 10 - 25 mg samples as are suggested in the prescribed method an additional residue from the ashless filter paper of 2×10^{-5} to 5×10^{-5} gm trapped with the platinum metal or occluded to the surface would be sufficient to cause results which are 0.2% high. Another possibility could involve slight oxidation of the platinum metal during the ignition process.

The first hypothesis could be tested by using larger samples of stock platinum solutions with proportionately larger additions of thiophenol. The second hypothesis could be tested by heating the platinum varying lengths of time after combustion to the metal is complete, or by heating in an atmosphere of hydrogen.

Table II - CONCENTRATIONS OF PLATINUM (IV) AND PLATINUM (II) SOLUTIONS

SOLUTION	CONCENTRATION
Stock Pt (IV)*	0.952 ± .003 mg/ml
Stock Pt (II)*	0.967 ± .002 mg/ml
Dilute Pt (IV)	0.0286 ± .0001 mg/ml
Dilute Pt (II)	0.0291 ± .0001 mg/ml

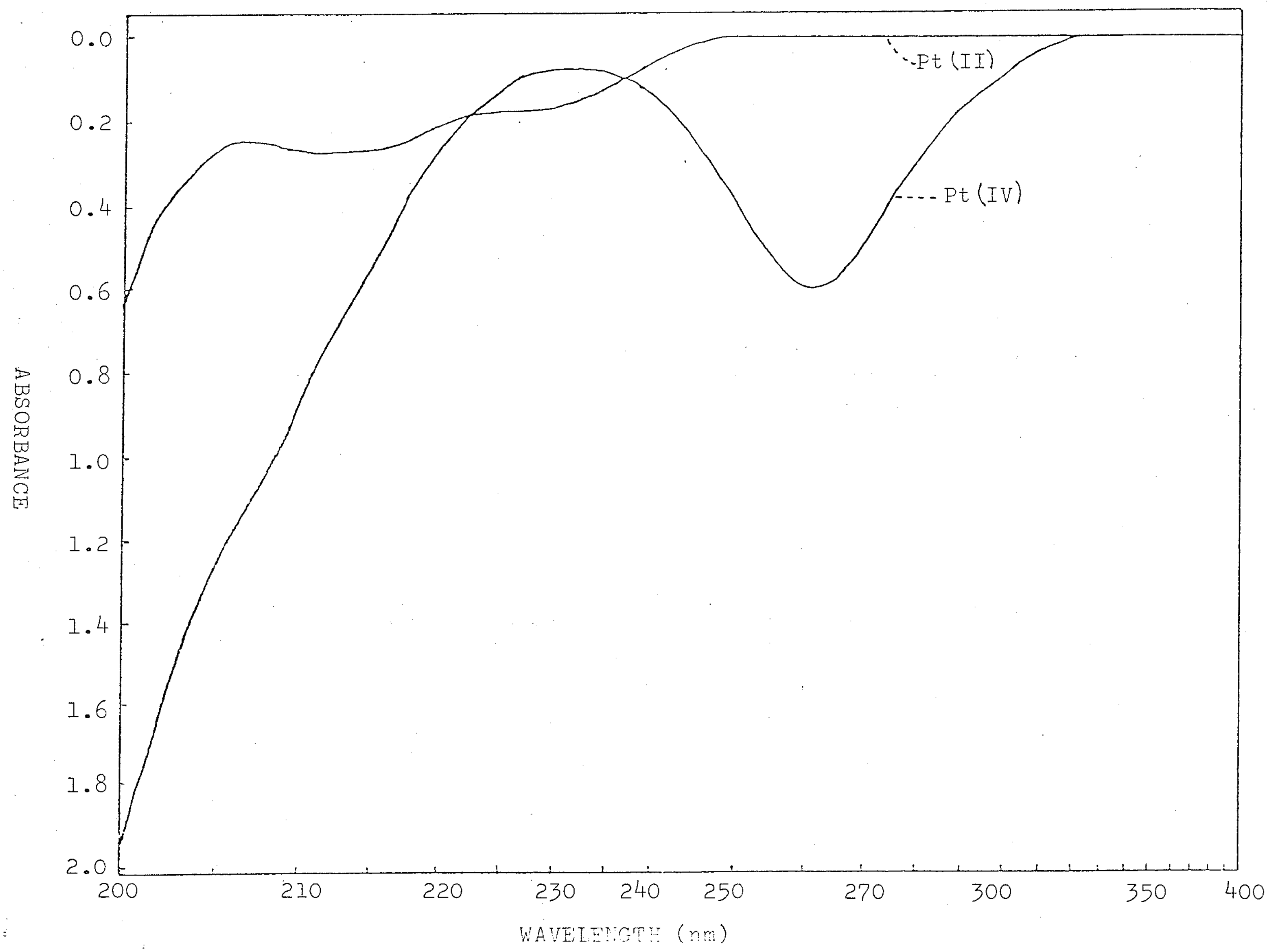
*Precipitation with thiophenol

D. Electronic Spectra of Platinum(IV) and Platinum(II)

The electronic spectra for the platinum(II) and platinum(IV) chloride solutions were taken between 400 and 200 nm (fig 1). The platinum(IV) solution showed an absorbance maximum at 262 nm in agreement with Vorlicek and Dolezal.[23] The platinum(II) solution showed no absorbance at 262 nm but there were two small maxima at 230 and 215 nm. The positions of all maxima corresponded very well with those reported by Elding and Leden.[24]

Figure 1

Electronic Spectra of $PtCl_4^{-2}$ and $PtCl_6^{-2}$
Pt = 6.96 ppm


0.0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
1.8
2.0
ABSORBANCE
200
210
220
230
240
250
270
300
350
400
WAVELENGTH (nm)
Pt(II)
Pt(IV)

E. Spectrophotometric Standardization For Platinum

All complex preparations were done in a manner similar to the method of Berman and Goodhue[1] which allowed the most sensitive spectrophotometric platinum determination by using the complex absorption at 310 nm. Since this study of the complex was done with the hope that it might eventually lead to an improved spectrophotometric determination for platinum, the complex absorption at 310 nm became a focal point of much of the spectrophotometric work.

Experimental

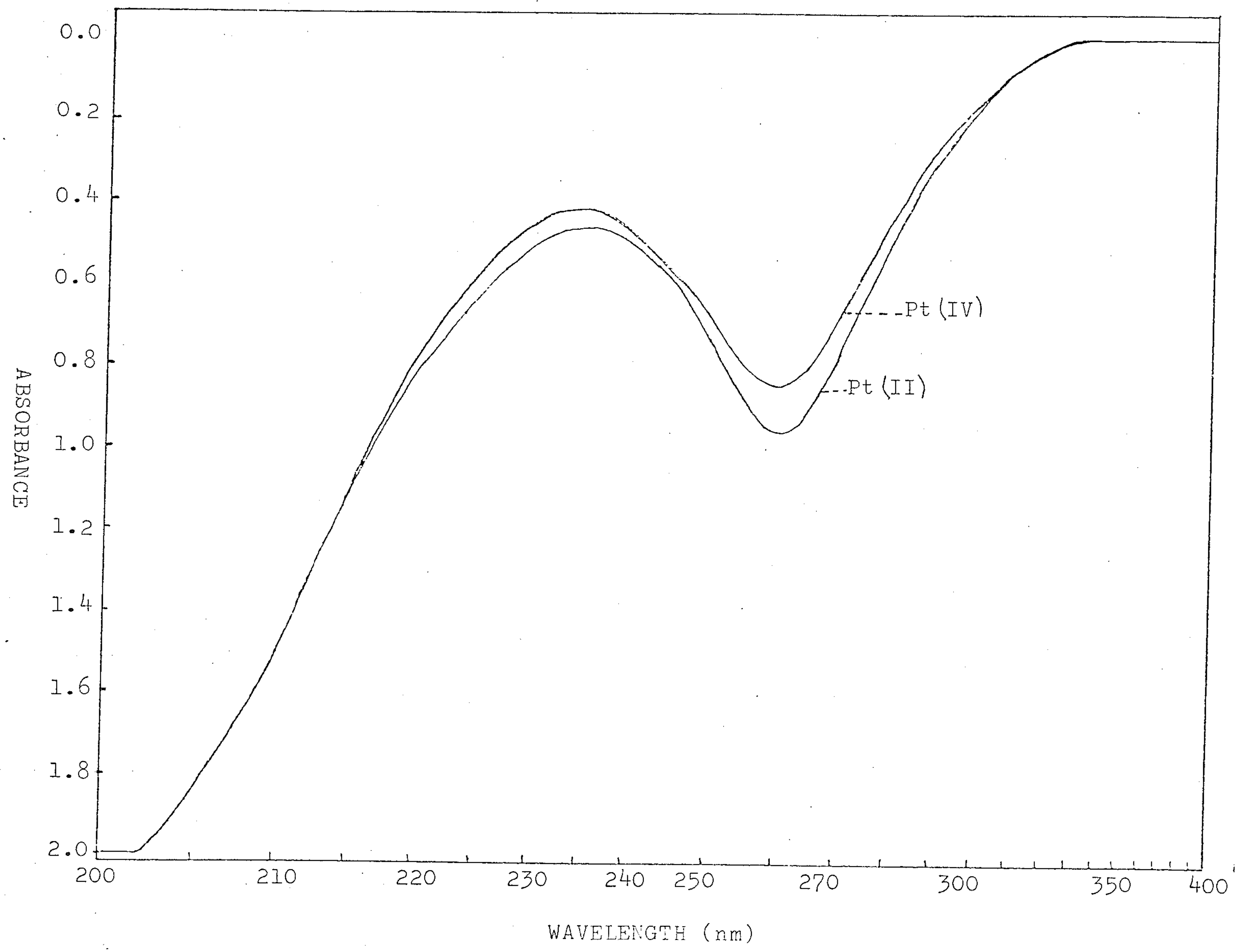
A volume of dilute platinum(IV) or platinum(II) stock solution ranging from 1.0 to 30.0 ml was placed in a beaker. 5.0 ml of concentrated hydrochloric acid were added and then 6.0 ml of concentrated sulphuric acid were added, carefully avoiding spattering. The solution was heated to just before sulphuric acid fumes and then allowed to cool. The remaining solution was transferred quantitatively to a calibrated 25.0 ml volumetric flask and 5.0 ml of concentrated perchloric acid were added. For complex formation the volumetric flask was then made to the mark by adding tin(II) chloride solution and water.

In the initial studies samples were prepared without tin(II) chloride and some samples were prepared excluding tin(II) chloride and perchloric acid.

Figure 2

Electronic Spectra of Solutions Prepared from
$PtCl_4^{-2}$ and $PtCl_6^{-2}$ using HCl, H_2SO_4
and $HClO_4$ with no $SnCl_2$ present

Pt(IV) = 9.28 ppm
Pt(II) = 9.55 ppm


0.0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
1.8
2.0
ABSORBANCE
200
210
220
230
240
250
270
300
350
400
WAVELENGTH (nm)
Pt(IV)
Pt(II)

Results

The electronic spectra of the platinum solutions prepared by the above method with the exclusion of the tin(II) chloride solution showed maximum absorbance at 260 nm for solutions prepared from dilute stock solutions of platinum(IV) and platinum(II) (fig 2). The platinum(II) solution showed a slightly stronger absorbance at 260 nm than the platinum(IV) solution and since equal volumes of dilute stock solutions were used for the platinum(II) and platinum(IV) samples, this stronger absorbance indicates that platinum(II) was completely oxidized to platinum(IV) by this method of sample preparation. Electronic spectra for samples prepared without either tin(II) chloride or perchloric acid showed no absorption at 260 nm when using dilute platinum(II) stock solution. Concentrated (150 ppm platinum) samples of platinum(II) showed a definite colour change to the bright yellow of platinum(IV) solutions immediately upon addition of concentrated perchloric acid. These results lead to the conclusion that perchloric acid rapidly and oxidizes platinum(II) to platinum(IV) and when using Berman and Goodhue's method the complex is always prepared by starting with platinum in an oxidation state of four.

Experimental

Platinum samples were prepared in the manner described above for complex formation. Three platinum samples and three blanks were prepared for each concentration of platinum. The tin(II) chloride was prepared by dissolving mossy tin as described above and was prepared at such concentrations that 5.0 ml of tin(II) chloride solution in the sample would provide a tin to platinum molar ratio of approximately 50/1. Samples containing 1.16 ppm to 11.6 ppm platinum were prepared by using the dilute platinum(IV) stock solution directly and the samples containing 0.29 ppm and 0.51 ppm platinum were prepared by successive dilutions of the dilute platinum(IV) stock solution. Each sample's absorbance was measured at 403 nm and 310 nm against a reagent blank prepared simultaneously with the sample excluding only the platinum.

Results

The results are presented in table 3 and Beer's Law plots were constructed giving a graphical presentation in figures 3 and 4.

Discussion

The large excess of tin(II) chloride used in this study was to assure complete colour development of the complex. At 310 nm and 403 nm, the most prominent maxima for the complex, the absorbance due to tin(II) chloride was zero.

As can be seen from figure 3 Beer's Law is adhered to reasonably well from 0.0 to 6.0 ppm as reported by Berman and Goodhue.[1] The molar absorptivity was found to be 3.20×10^4 considering 7 points from 0.00 ppm to 5.80 ppm or 3.88×10^4 considering 5 points from 0.00 ppm to

2.32 ppm as compared to 3.95×10^4.[1] At higher platinum concentrations the decrease in molar absorptivity showed that the absorbance at 310 nm has a very limited range when applied to accurate quantitative determination of platinum. This deviation from Beer's Law may indicate dissociation of the complex with possible reassociation of a complex absorbing at another wavelength. Further spectrophotometric studies were undertaken to test this hypothesis; however at tin to platinum ratios of 50/1 the deviation from linearity should not really involve complex dissociation according to Young *et al*.[15] Another possible reason for this deviation from linearity for the absorption at 310 nm after 6.0 ppm platinum might involve non-linear instrument response past an absorbance of 1.00, but this would seem unlikely also. The upper limit of linear response for the absorption at 310 nm was reported as 6.0 ppm by Berman and Goodhue,[1] the same limit found in the present study.

Figure 4 shows that the absorbance for the complex at 403 nm, although a somewhat less sensitive measure of the concentration of the platinum, adheres to Beer's Law very well from 0.0 ppm to 12.0 ppm. The molar absorptivity corresponded quite well with previously reported values, 8.07×10^3 as compared to 7.83×10^3.[3]

The data for the absorbance at 310 nm was plotted by using the least squares best fit technique for the points from 0.00 to 5.80 ppm platinum. The data for the absorbance at 403 nm was plotted in a similar manner for the points from 0.00 to 11.6 ppm platinum.

Table III - ABSORBANCE VERSUS PLATINUM CONCENTRATION FOR THE PLATINUM - TIN(II) CHLORIDE COMPLEX

CONCENTRATION	ABSORBANCE	
Pt (ppm)	310 nm	403 nm
0.00	0.00	0.00
0.29	0.048*	
0.58	0.081*	
1.16	0.241	0.056
2.32	0.448	0.114
4.64	0.795	0.204
5.80	0.93	0.245
6.96	1.07	0.300
9.28	1.28	0.408
11.6	1.47	0.478

*4.0 cm cells with a tin to platinum molar ratio of approximately 200/1. The absorbance has been corrected to a 1.0 cm path length. All other samples were measured in a 1.0 cm cell.

Figure 3

Beer's Law Plot of Absorbance at 310 nm
Versus Platinum Concentration
$[\mathrm{Sn\ (II)}] = 6 \times 10^{-2}$ M

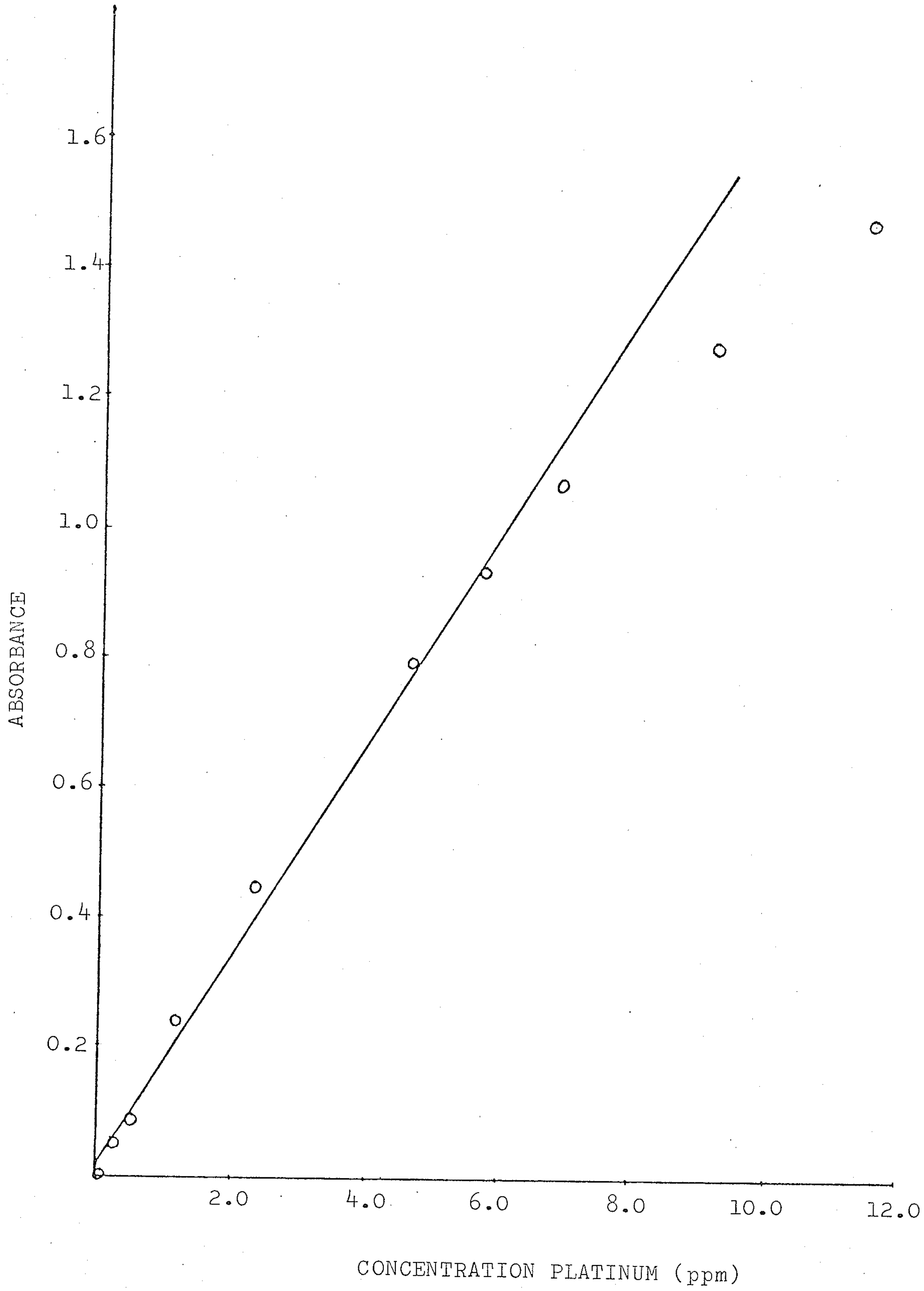
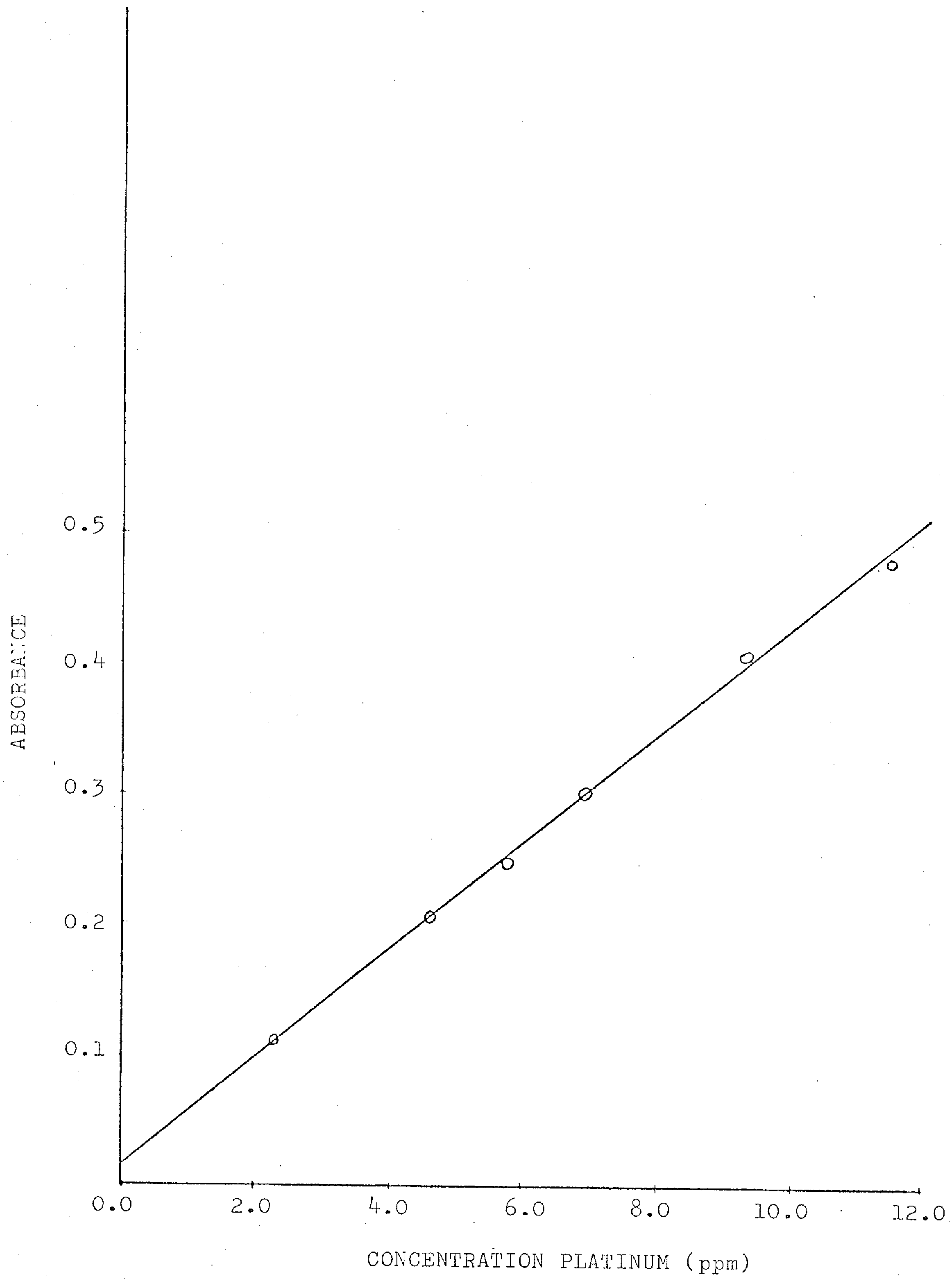

ABSORBANCE
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
2.0
4.0
6.0
8.0
10.0
12.0
CONCENTRATION PLATINUM (ppm)

Figure 4

Beer's Law Plot of Absorbance at 403 nm
Versus Platinum Concentration
$[\mathrm{Sn(II)}] = 6 \times 10^{-2}$ M


ABSORBANCE
0.5
0.4
0.3
0.2
0.1
0.0
2.0
4.0
6.0
8.0
10.0
12.0
CONCENTRATION PLATINUM (ppm)

V. Spectrophotometric Study of the Oxidation State of Platinum in the Complex

Determining the tin to platinum ratio in the complex depends completely on knowing whether platinum(IV) is reduced by tin(II) chloride to platinum(II) or platinum (0), or if platinum(IV) is reduced at all in a perchloric acid medium. A study was designed to determine the oxidation state of platinum in the complex. The study involved varying the tin concentration in a sample of fixed platinum concentration and observing the effects on the electronic spectrum between 200 nm and 400 nm.

Experimental

For this work eight identical platinum samples were prepared simultaneously using the modified method of Berman and Goodhue described above. Fresh tin(II) chloride solutions were prepared for each concentration of platinum, at concentrations which would allow convenient additions to the platinum samples to yield small whole number molar ratios between the tin and platinum. The electronic spectra were obtained using a Perkin Elmer 450 spectrophotometer.

Results

The results of the study are presented in tables IV, V and VI and representative spectra presented in figures 5, 6, 7 and 8.

Discussion

One observation which came from this study was that even slight fuming of the sulphuric acid during the preparation of the platinum samples can lead to very erratic results as was evidenced with the eighth sample of the series recorded in table IV. At a tin to platinum ratio of 50/1 for the fumed sample the absorbances were $A(254) = 0.88$ and $A(310) = 0.85$. It should be noted that these absorbances are considerably lower than those for the sample with tin to platinum ratios of 40/1. These low absorbances were also reported by Berman and Goodhue[1] with no explanation.

When the platinum sample is being prepared, the heating after addition of the hydrochloric acid and sulphuric acid causes the removal of the hydrochloric acid and a large percentage of the water by evaporation. As the heating continues, if left unchecked, the sulphuric acid starts to fume. The resulting fog or mist of sulphur trioxide and water vapor is viewed by this author as being able to transport some of the platinum from the solution to the sides of the beaker and watch glass covering. The platinum which is trapped in a sulphur trioxide film is not transferred from the beaker quantitatively with water due to the low solubility of sulphur trioxide in water. Berman and Goodhue's[1] observation that adding more sulphuric acid regenerates the complex absorbance is in agreement with this proposal as well. Since sulphur trioxide is highly soluble in sulphuric acid washing with the acid should release the platinum.

The more obvious proposal would have been to suggest that there is some form of complex change after fuming the sulphuric acid; however the only change in the electronic spectrum is in intensity, not absorption maxima positions and this proposal has to be discounted.

Since the present study only required reproducibility between samples and this can be assured even after fuming of the sulphuric acid by merely adding more sulphuric acid no further studies were done in this respect.

Table IV - ELECTRONIC SPECTRA OF A PLATINUM* (IV) SOLUTION WITH ADDITIONS OF VARYING AMOUNTS OF TIN** (II) CHLORIDE SOLUTION

$SnCl_2$ ADDED	APPROXIMATE Sn/Pt MOLAR RATIO	ABSORBANCE MAXIMA	DESCRIPTION OF SPECTRA
0.0 ml		260 nm	A =0.52
0.2 ml	2/1	260 nm	A =0.39 maximum reduced
0.5 ml	5/1	230 nm	very small maximum
		254 nm	very small maximum - no evidence of maximum at 260 nm
1.0 ml	10/1	254 nm	A =0.31 fairly prominent maximum
		310 nm	A =0.20 evidence of maximum - faint suggestion of shoulders at 230 nm and 273 nm
2.0 ml	20/1	254 nm	A =0.82 distinct maximum
		310 nm	A =0.66 distinct maximum
		273 nm	a shoulder appearing
3.0 ml	30/1	254 nm	A =0.96
		310 nm	A =0.91
		273 nm	- shoulder A =0.80
4.0 ml	40/1	254 nm	A = 1.02
		310 nm	A = 0.94
		273 nm	- shoulder A =0.84
5.0 ml⊕	50/1	254 nm	A =0.88
		310 nm	A =0.85
		273 nm	- shoulder A =0.72

*[Pt] = 5.80 ppm
= 7.43×10^{-7} moles/25 ml sample
**[Sn(II)] = 7.20×10^{-6} moles/ml
⊕ fumed sample

Table V - ELECTRONIC SPECTRA OF A PLATINUM* (IV) SOLUTION WITH ADDITIONS OF VARYING AMOUNTS OF TIN**(II) CHLORIDE SOLUTION

$SnCl_2$ ADDED	APPROXIMATE Sn/Pt MOLAR RATIO	ABSORBANCE MAXIMA	DESCRIPTION OF SPECTRA
0.0 ml		260 nm	A =0.96
0.2 ml	1/1	260 nm	A =0.51 maximum reduced
0.5 ml	2.5/1	230 nm	A =0.30 - no evidence of absorption at 260 nm
1.0 ml	5/1	254 nm	A =0.58
		310 nm	A =0.21
		230 nm	slight shoulder
		273 nm	slight shoulder
2.0 ml	10/1	254 nm	A = 1.51
		310 nm	A = 1.21
		273 nm	slight shoulder - no shoulder at 230 nm
3.0 ml	15/1	254 nm	A greater than 2.00
		310 nm	A = 1.82
		273 nm	shoulder is more prominent
4.0 ml	20/1	254 nm	A greater than 2.00
		310 nm	A = 1.98
		273 nm	prominent shoulder

*[Pt] = 11.6 ppm
= 1.49×10^{-6} moles/25 ml sample
**[Sn(II)] = 7.12×10^{-6} moles/ml

Table VI - ELECTRONIC SPECTRA OF A PLATINUM* (IV) SOLUTION WITH ADDITIONS OF VARYING AMOUNTS OF TIN**(II) CHLORIDE SOLUTION

$SnCl_2$ ADDED	APPROXIMATE Sn/Pt MOLAR RATIO	ABSORBANCE MAXIMA	DESCRIPTION OF SPECTRA
0.0 ml		260 nm	A = 1.87
0.5 ml	1.25/1	260 nm	A ≐0.32 - no evidence of any other absorption from 200 nm to 400 nm which could relate to the platinum or the complex
1.0 ml	2.5/1	254 nm	A =0.62
		310 nm	A =0.15
		273 nm	slight shoulder
1.5 ml	3.75/1	254 nm	A = 1.13
		310 nm	A = 0.61
		273 nm	slight shoulder
2.0 ml	5.0/1	254 nm	A = 1.78
		310 nm	A = 1.04
		273 nm	slight shoulder
2.5 ml	6.25/1	254 nm	A greater than 2.00
		310 nm	A = 1.61
		273 nm	shoulder clearly evident
3.0 ml	7.5/1	254 nm	A greater than 2.00
		310 nm	A greater than 2.00

*[Pt] = 23.2 ppm
= 2.97×10^{-6} moles/25 ml sample
**[Sn(II)] = 7.20×10^{-6} moles/ml

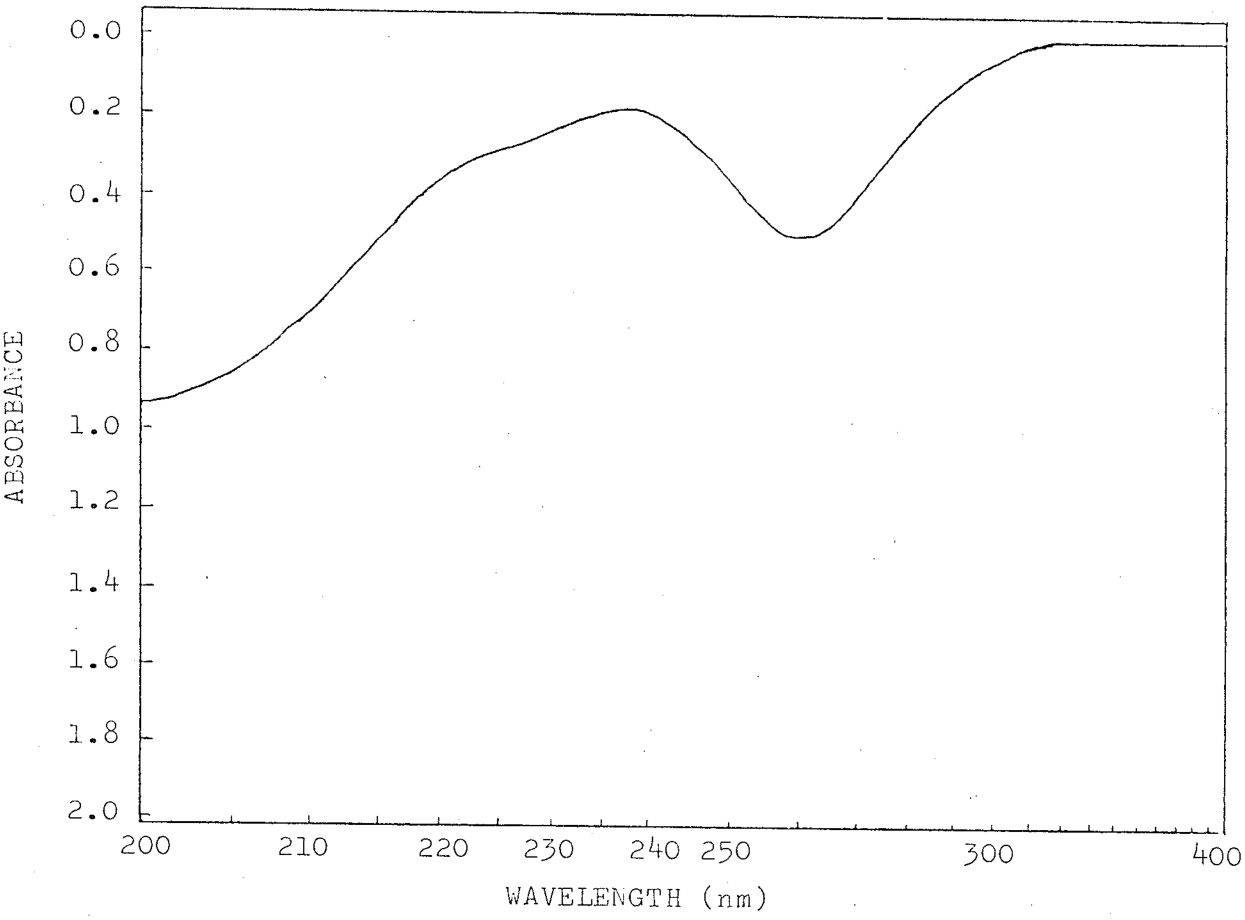
Figures 5 and 6 are representative of the electronic spectra of a solution 11.6 ppm platinum prepared by the method of Berman and Goodhue[1] with tin(II)chloride to platinum molar ratios as indicated.

Figure 5

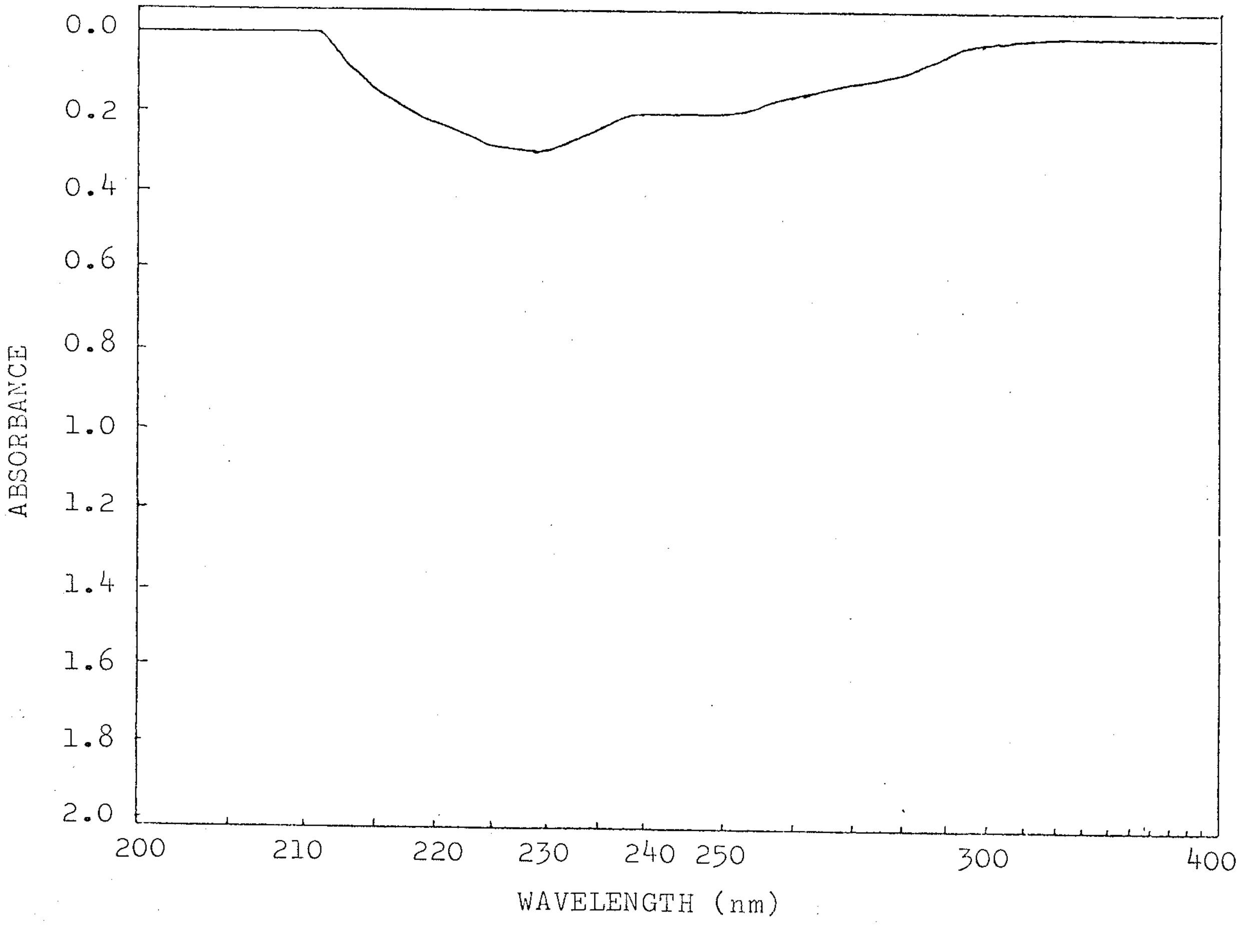
Tin(II) to Platinum = 1/1

Figure 6

Tin(II) to Platinum = 2.5/1



ABSORBANCE
0.0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
1.8
2.0
200
210
220
230
240
250
300
400
WAVELENGTH (nm)



ABSORBANCE
0.0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
1.8
2.0
200
210
220
230
240
250
300
400
WAVELENGTH (nm)

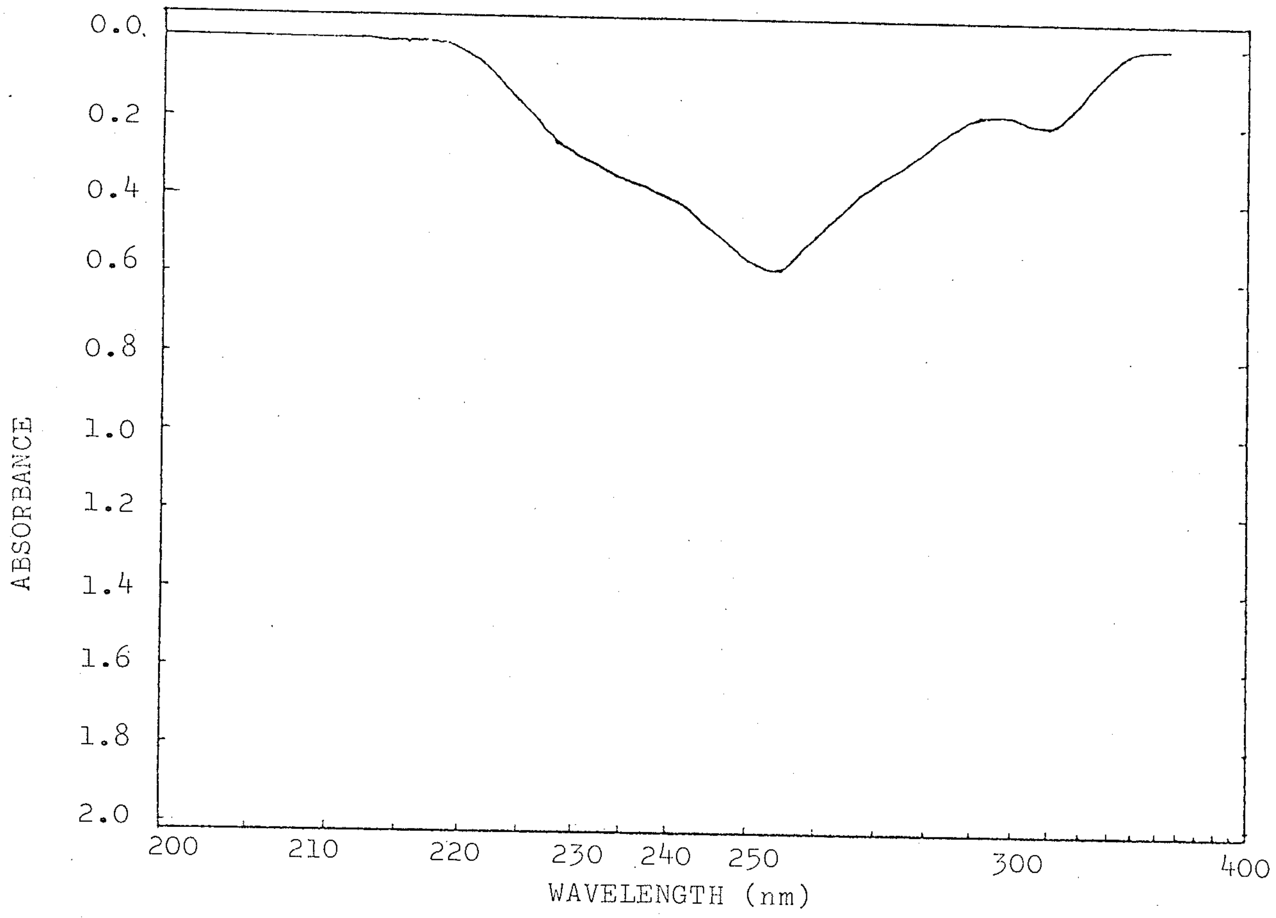
Figures 7 and 8 are representative of the electronic spectra of a solution 11.6 ppm platinum prepared by the method of Berman and Goodhue[1] with tin(II) chloride to platinum ratios as indicated.

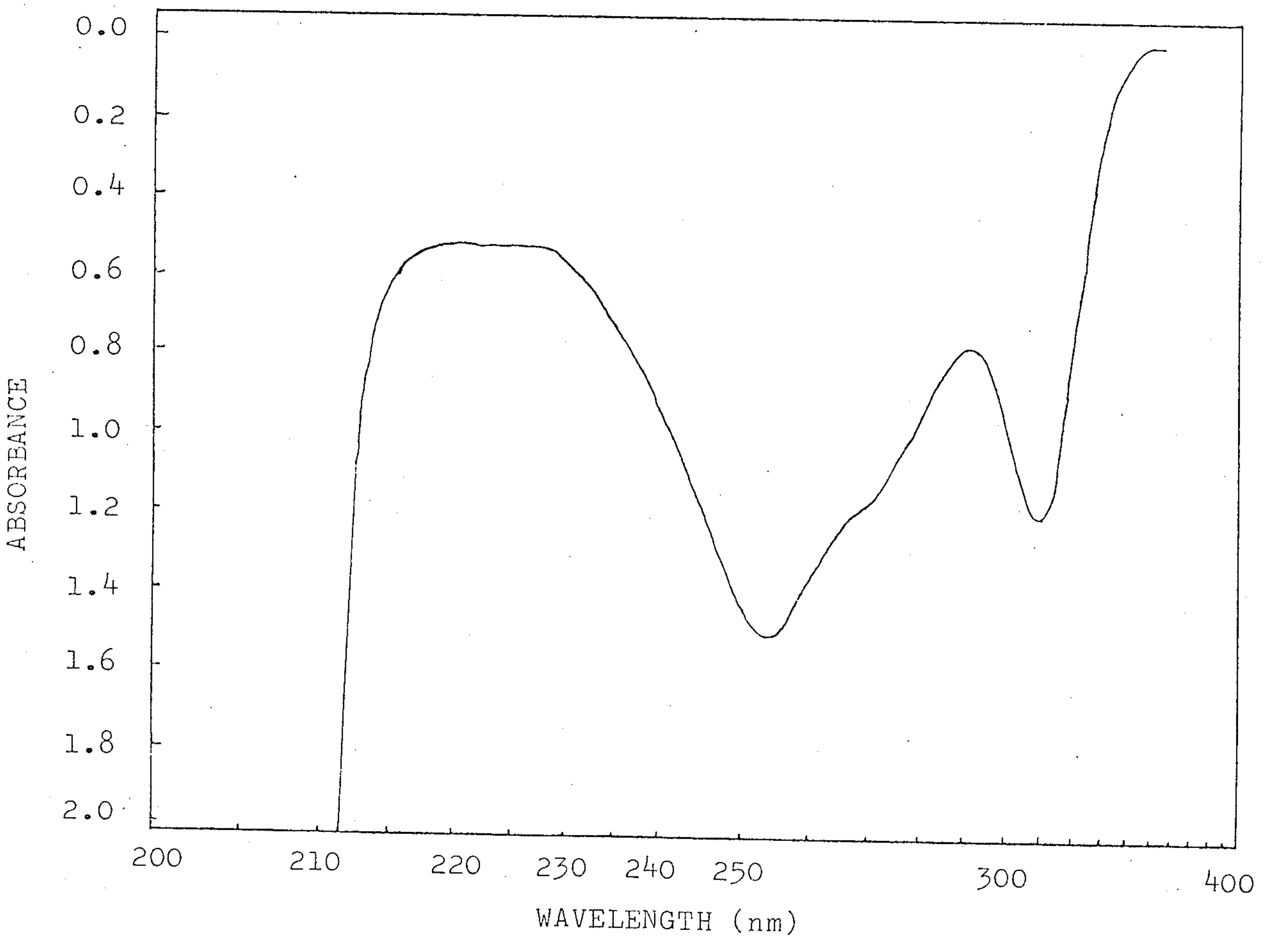
Figure 7

Tin(II) to Platinum = 5/1

Figure 8

Tin(II) to Platinum = 10/1


0.0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
1.8
2.0
ABSORBANCE
200
210
220
230
240
250
300
400
WAVELENGTH (nm)


0.0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
1.8
2.0
ABSORBANCE
200
210
220
230
240
250
300
400
WAVELENGTH (nm)

Tables IV, V and VI provide qualitative data only. Since the purpose of this study was to search for evidence for reduction of platinum (IV), each set of samples was run against only one reagent blank. The reagent blank was only used to set the zero absorbance. This accounts for the unusually high absorbances at tin to platinum molar ratios of 20/1 and 7.5/1 in tables V and VI respectively. It should also be noted that as the tin to platinum molar ratio increased the spectra were measured only between 200 nm and 350 nm because of an interfering peak at 403 nm due to the complex. Omitting 403 nm from the study is acceptable as it essentially reflects the absorbance at 310 nm only at 25% of the sensitivity. The range from 200 nm to 350 nm includes the region used to identify platinum (IV) and platinum (II).

Considering table V and figures 5 and 6 it can be seen quite readily that as tin (II) chloride is added to a solution containing platinum (IV) with an absorbance maximum at 260 nm (fig 5) the absorbance at 260 nm decreases and platinum (II) is produced with an absorbance maximum at 230 nm (fig 6).

This spectrophotometric study also allows continuous examination of the state of the system and by considering the tin to platinum molar ratios at the first appearance of electronic absorption due to the complex, there is evidence suggesting the further reduction of platinum to the zero valent state.

If one considers the trend in the first appearance of the shoulder at 273 nm which is associated with the complex formation it appears at a tin to platinum ratio of 10/1, 5/1, and 2.5/1 for platinum concentrations of 5.80 ppm (table IV), 11.6 ppm (table V), and 23.2 ppm (table VI) respectively. This shoulder also becomes more well defined as the tin to platinum ratio increases. Based on this trend one is led to suggest that the low concentrations of platinum and tin have a considerable effect on the complex forming equilibrium. Considering also the fact that as the tin to platinum ratio increases from 15/1 to 20/1 (table V) the absorbance due to the complex also increases it can be seen that the equilibrium requires a large excess of tin (II) to drive the reaction to completion. Therefore in the present study at very low platinum and tin concentrations (6 - 12 ppm) absorbance due to the complex is not even observed until a tin to platinum molar ratio of greater than 5/1 is achieved.

On the basis of this suggestion it is concluded that the results of tables IV and V show only that reduction of platinum (IV) is necessary before complex formation and that the results of table VI might more clearly represent the stoichiometry of this reduction before complexation begins. Since at low platinum and tin concentrations the reactions are less complete, it is possible to observe peaks at 230 nm in the electronic spectrum which correspond to platinum (II). The suggested reduction is:

$$\text{Pt(IV)} + \text{Sn(II)} \longrightarrow \text{Pt(II)} + \text{Sn(IV)}$$

The disappearance of the absorption at 260 nm which is associated with platinum (IV) also supports this suggested reduction.

At higher platinum (23.2 ppm) and tin concentrations the reaction is much more complete and although the absorption at 230 nm is not observed the disappearance of the absorption at 260 nm also suggests that the above reduction occurs. However, there is no absorption which can be attributed to complex formation until the tin to platinum molar ratio is in the range 1.25/1 to 2.5/1. This would seem to allow the possibility of the further reduction

$$\mathrm{Pt(II)} + \mathrm{Sn(II)} \longrightarrow \mathrm{Pt\ (0)} + \mathrm{Sn(IV)}$$

Conclusions

The spectrophotometric studies were not conclusive regarding the reduction of platinum to the zero valent state as no tests were made to assure that at a concentration of 23.2 ppm platinum, complete reduction to platinum (0) occurred before complexation began. In fact it can be seen from table V (tin to platinum - 5/1) that absorption due to platinum(II) at 230 nm can be observed after complex formation has begun.

These studies do show conclusively however that platinum(IV) is reduced to platinum(II) or platinum (0) before complexation occurs.

Other Studies

A similar study has since been published by Elizarova and Matvienko[8] and as has been the case in studies of this complex, agreement is not complete. These authors used K_2PtCl_4 as their source of platinum and chose to prepare the platinum - tin(II) chloride complex in a solution of a constant ionic strength of two. In order to maintain this constant ionic strength perchloric acid was added to the chloride medium. In another piece of work by Elizarova and Matvienko[9] also published after the present study was completed they suggested that, based on potentiometric and polarographic studies, tin(II) chloride reduces platinum to a zero valent state. In both studies[8,9] K_2PtCl_4 was used and the platinum was assumed to be in the form of platinum(II). In both studies the reduction

$$\text{(A)}\quad \mathrm{Pt(II)} + \mathrm{Sn(II)} \longrightarrow \mathrm{Pt\ (O)} + \mathrm{Sn(IV)}$$

was assumed and in their spectrophotometric studies[8] the tin(II) required for this reduction is subtracted from the tin(II) added in order to predict ratios of tin to platinum of 2/1 and 1/1 in the complexes.

However, it has been shown clearly in the present study that addition of perchloric acid to a platinum(II) solution causes immediate and complete oxidation of the platinum to platinum(IV) (fig 2). Elizarova and Matvienko failed to consider this oxidation by perchloric acid and as a result did not consider the reduction of platinum(IV) to platinum(II) in their studies. If Elizarova and Matvienko's tin to platinum ratios of 2/1 and 1/1 in the complex are correct, instead of the reduction (A) the only reduction actually occurring is

$$\text{(B)}\quad \mathrm{Pt(IV)} + \mathrm{Sn(II)} \longrightarrow \mathrm{Pt(II)} + \mathrm{Sn(IV)}$$

and the complex is a complex involving platinum (II). On the other hand if they are correct concerning the zero valent state of the platinum in the complex the reduction involved should be

$$\text{(C)} \quad Pt(IV) + 2Sn(II) \longrightarrow Pt(0) + Sn(IV)$$

and one unit of tin should be subtracted from their predicted ratios for the tin to platinum in the complex, thus giving 1/1 and 0/1. This second ratio would then involve no complex formation. If one does consider the platinum in the complex to be in a zero valent state, the work of Elizarova and Matvienko[8,9] appears rather suspect.

In order to further examine this possibility of reduction of platinum to the zero valent state a series of polarographic studies were undertaken.

VI. Polarographic Studies to Determine the Oxidation State of Platinum in the Platinum - Tin(II)Chloride Complex

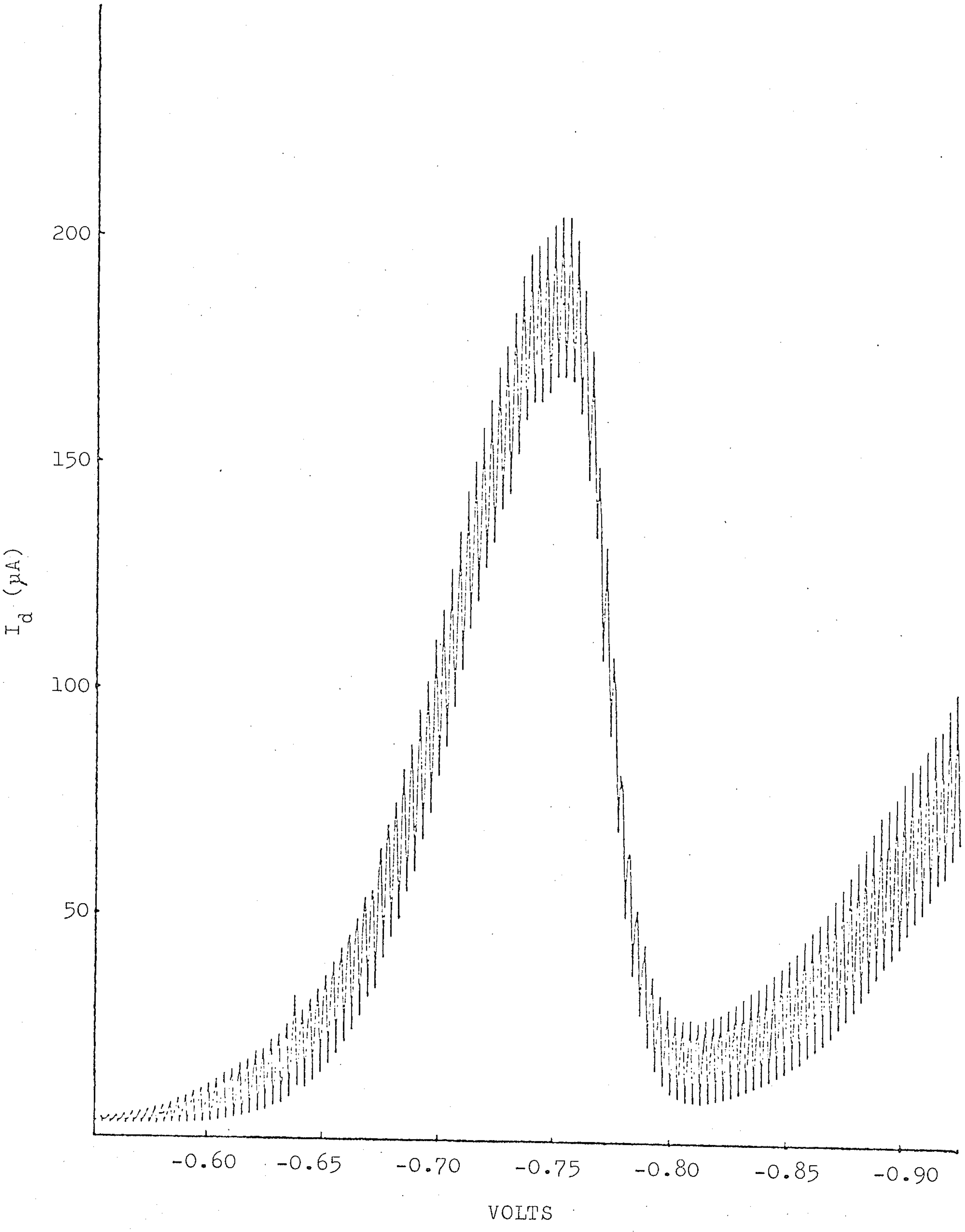
A. Determination of the Study Parameters

Several investigators[25,26] have studied the polarographic reduction of platinum(II) and platinum(IV) at a dropping mercury electrode. The polarographic waves are definitely not suited to quantitative study but are reported to have a peculiar characteristic of a maximum and minimum in the diffusion current (fig 9). The present work utilizes this maximum-minimum type of wave for platinum(IV) and by the nature of the study some quantitative conclusions can be made.

Platinum solutions were prepared exactly as was described in the spectrophotometric studies, and to serve as a supporting electrolyte 20.0 ml of a solution 0.5 M in sodium chloride and 2.0 M in perchloric acid were added to make a total volume of 45.0 ml per sample. No tin(II)chloride was included in the sample preparation. The procedure involved deaerating the 45.0 ml platinum samples by bubbling with nitrogen for fifteen minutes. The samples were then maintained under a nitrogen atmosphere to reduce the effects of any complex instability when in contact with air. The tin(II)chloride solutions were prepared fresh daily as described earlier and maintained under a nitrogen atmosphere. The tin(II)chloride solutions were prepared at such concentrations to allow convenient additions to the platinum sample so as to yield small whole number molar ratios between tin and platinum. After the sample was deaerated, the tin(II) chloride solution was added to the polarographic cell (fig 10) from a burette to perform an amperometric titration with simultaneous diffusion current measurements to monitor the increase in the concentration of the reducing and complexing agent, tin(II) chloride. After each addition of tin(II) chloride the samples were again bubbled with nitrogen to effect mixing and assure complete deaeration of the samples. The titration process progressed with regular addition of tin(II) chloride followed by nitrogen bubbling and polarographic scans.

Figure 9

Polarographic Wave for 3.31×10^{-5} M
Platinum(IV) Solution


200
150
100
50
I_d (μA)
-0.60
-0.65
-0.70
-0.75
-0.80
-0.85
-0.90
VOLTS

Experimental

All polarographic work was performed using the apparatus illustrated in figure 10. The right hand side of the cell contained a saturated calomel electrode as the reference electrode and electrical contact with the indicator electrode in the left-hand side of the cell was achieved using an agar, potassium chloride (1.02 M) salt bridge. The dropping mercury indicator electrode was adjusted to a drop rate of three seconds per drop for each trial. Deaeration was accomplished by bubbling nitrogen through the samples via the tube shown on the left of the reaction half-cell and the solutions were maintained under nitrogen by blowing nitrogen over the sample through the tube shown at the top of the reaction half-cell.

All polarographic studies were done at room temperature ($21 \pm 1^\circ$ C).

Figure 10

Polarographic Cell

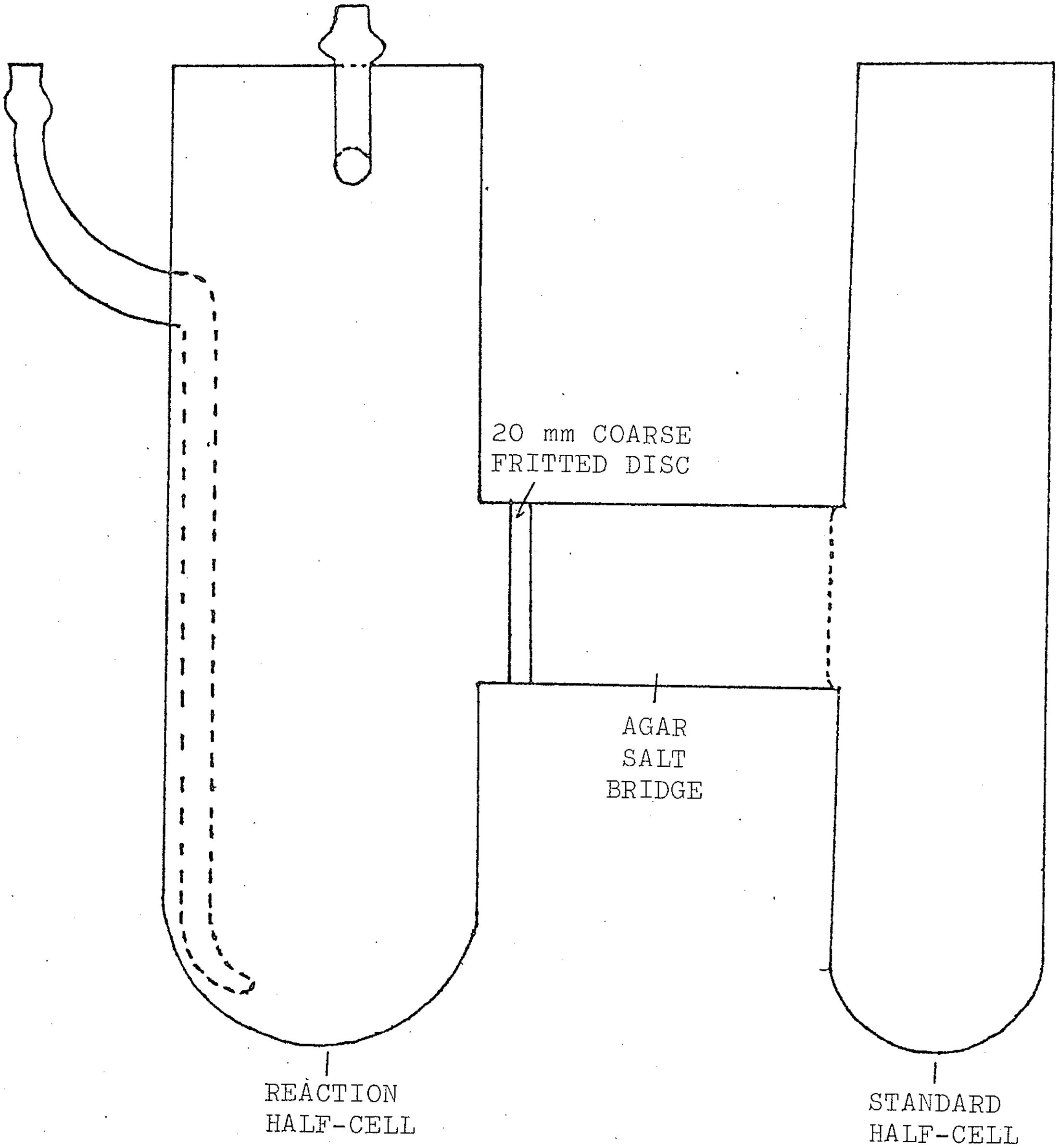


DIAGRAM TO SCALE

B. The Region of Polarographic Study

As there were no published reports on which to pattern this study, the optimum experimental conditions and parameters of study had to be established.

A polarographic scan of a reagent blank (fig 11) prepared as described above excluding platinum established the limits of the region of the study to -0.20V to -0.85V vs. S.C.E. The end of the wave due to anodic dissolution of mercury around 0.0V and the reduction of hydrogen ion beginning at -0.90V determined this region of study.

Figure 11

Polarogram of reagent blank with a sensitivity of 0.01 uA/mm

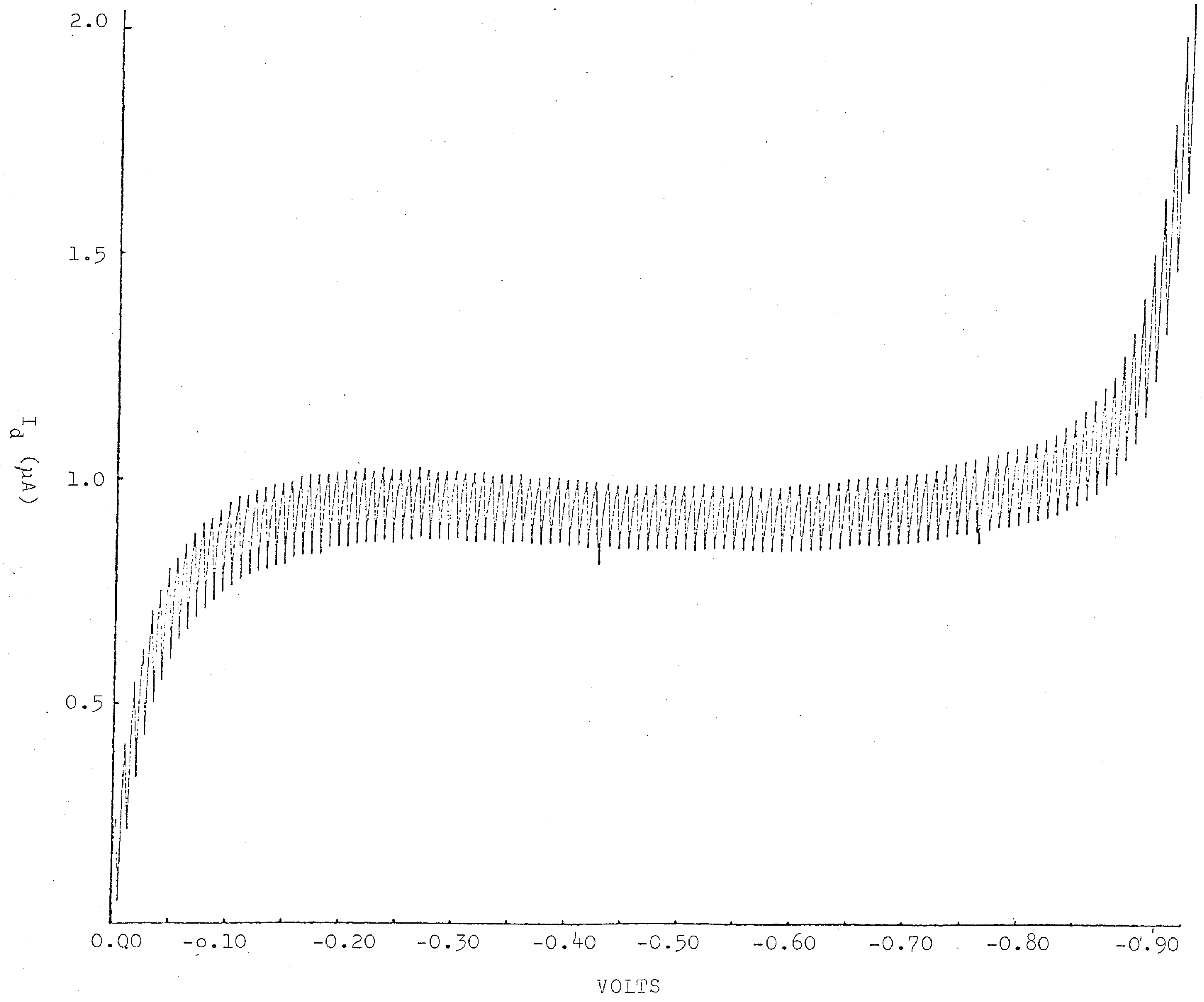

2.0
1.5
1.0
0.5
I_d (μA)
0.00
-0.10
-0.20
-0.30
-0.40
-0.50
-0.60
-0.70
-0.80
-0.90
VOLTS

Figure 12

Polarogram for 1.24 x 10^{-4} M tin(II)chloride solution.
Half-wave potential = -0.51V Sensitivity = 0.01 μA/mm

C. Polarographic Behaviour of Platinum(IV) Solutions

Preliminary scans in the region -0.20 to -0.85 vs. S.C.E. using platinum(IV) solutions prepared in the method described above gave polarograms with a form characterized in figure 9. Increasing platinum(IV) concentrations increased the maximum in the diffusion current, however this increase did not prove to be linear in respect to the platinum concentration. However, when one considers the scan of the reagent blank (fig 11) and the scan of the platinum(IV) solution (fig 9) the only difference is the presence of platinum(IV) in the latter case and the maximum must therefore be due to the platinum(IV). These preliminary studies on this maximum associated with platinum(IV) were done with five drops of 0.1% Triton X suppressor. A further study on the effects of the suppressor showed that zero to twenty drops had no effect on the maximum associated with platinum(IV). The diffusion current maximum was centered around -0.75V vs. S.C.E.

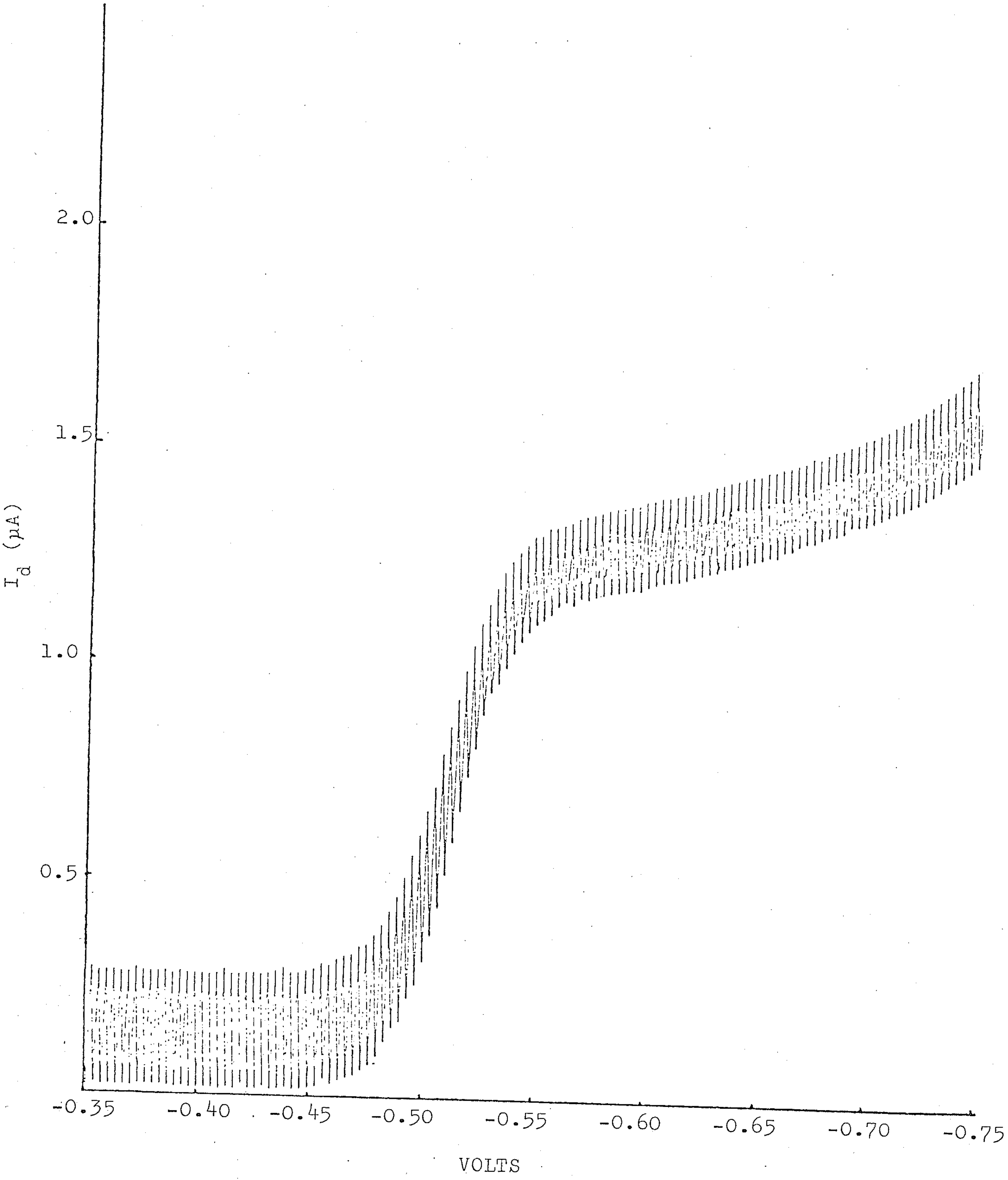
D. Polarographic Behaviour of Tin(II)Chloride

Initial tests in which tin(II) chloride was added to a reagent blank to give concentrations in the range of 10^{-4} to 10^{-5} M showed that five drops of suppressor were sufficient to suppress a maximum which appeared in the polarographic wave at the higher tin concentrations. A typical polarogram for tin(II) chloride is shown in figure 12.

Since the purpose of the work required an amperometric titration to follow the reduction of platinum(IV) and a simultaneous determination of tin(II) chloride in the presence of tin(IV) after the reduction of the platinum(IV), it was necessary to determine whether the polarographic wave due to tin(II) could be used for quantitative determinations and whether a tin(IV) wave interfered with a tin(II) polarographic wave.

Experimental

A 45.0 ml reagent blank was prepared as described above and a tin(II) chloride solution prepared and standardized iodometrically as 2.53×10^{-3} M. The reagent blank was deaerated by bubbling with nitrogen and five drops of 0.1% Triton X were added. The tin(II) chloride solution was added using a burette and polarographic scans were done from -0.20V to -0.85V.


2.0
1.5
1.0
0.5
I_d (μA)
-0.35
-0.40
-0.45
-0.50
-0.55
-0.60
-0.65
-0.70
-0.75
VOLTS

Results

The tin(II) concentrations were calculated considering the dilution effect after each addition to the 45.0 ml reagent blank.

$$\left[Sn(II)\right] = \frac{ML \times C}{ML + 45.0}$$

ML = ml of tin(II) chloride added
C = molar concentration of tin(II) chloride being added

The results are listed in table VII.

The half-wave potential was measured for each polarogram as -0.51 ± 0.005V by constructing the bisector of the angle formed between the residual and diffusion current plateaus and the diffusion current was measured at the half-wave potential as the vertical distance between the extrapolated residual and diffusion current plateaus as illustrated in figure 13. These results are also listed in table VII.

A plot of diffusion current versus molar tin(II) chloride concentration is shown in figure 14. The average slope of the plot was determined as $\overline{X}$ calculated as:

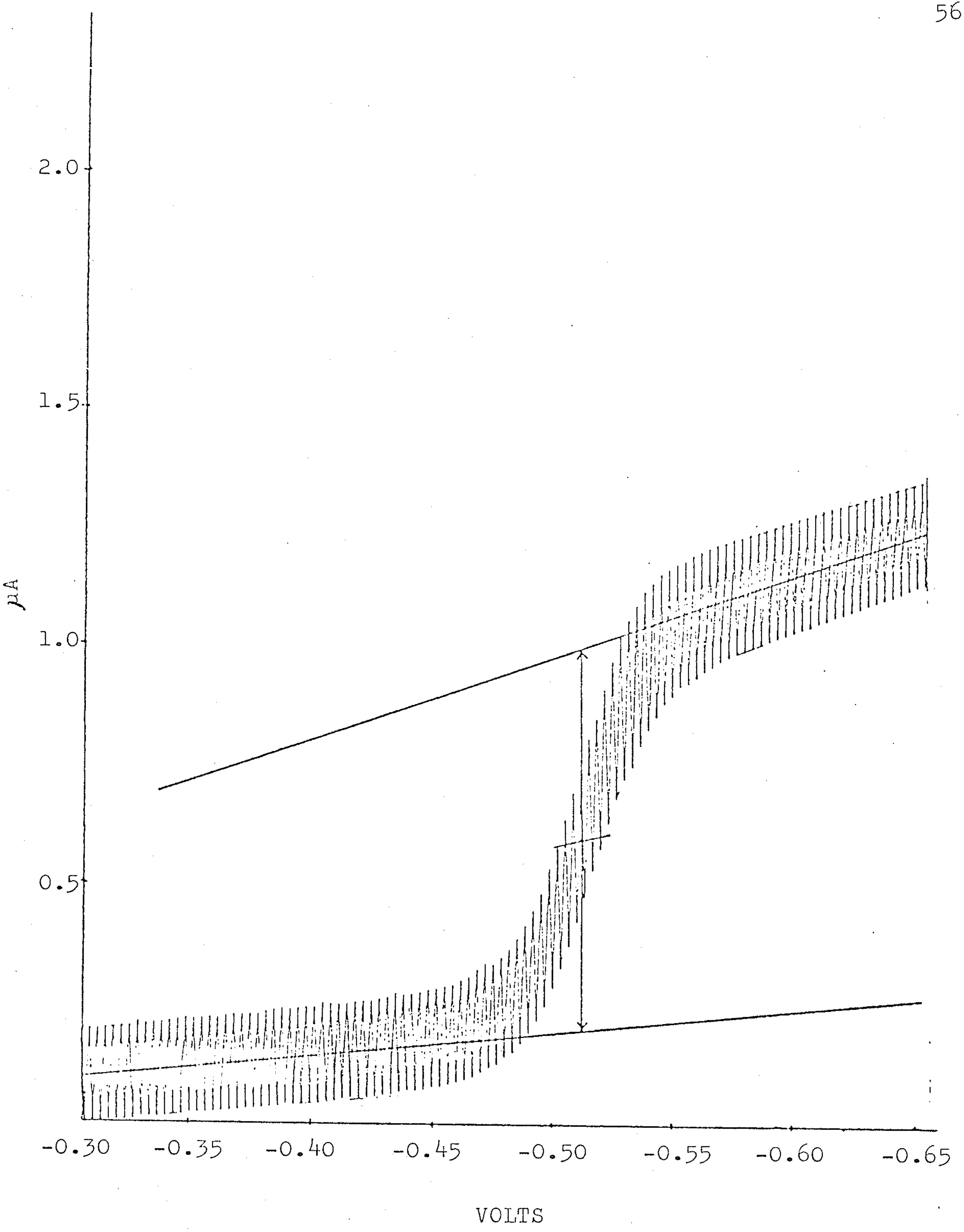
$$\text{(D)} \qquad \overline{X} = \frac{\displaystyle\sum_{n=1}^{a-1}\left[\frac{\displaystyle\sum_{i=1}^{a-n}\left(\frac{C_{n+i} - C_n}{M_{n+i} - M_n}\right)}{(a-n)}\right]}{a-1}$$

Table VII - POLAROGRAPHIC TIN (II) CHLORIDE STANDARD

ml $SnCl_2$ ADDED	MOLAR CONCENTRATION Sn (II)	I_d (µA)
0.00	0.00	0.00
0.80	2.99×10^{-5}	0.274
1.00	3.72×10^{-5}	0.311
1.50	5.52×10^{-5}	0.477
2.00	7.29×10^{-5}	0.645
2.50	9.01×10^{-5}	0.774
3.00	1.07×10^{-4}	0.915
3.50	1.24×10^{-4}	1.08
4.00	1.40×10^{-4}	1.20
4.50	1.56×10^{-4}	1.35
5.00	1.71×10^{-4}	1.47
6.00	2.01×10^{-4}	1.72

Figure 13

Measurement of Half-Wave Potential and Diffusion Current for Tin(II) Chloride


2.0
1.5
1.0
0.5
μA
-0.30
-0.35
-0.40
-0.45
-0.50
-0.55
-0.60
-0.65
VOLTS

a = number of plotted points

C_n = diffusion current measured at -0.51V for the n^{th} addition of tin(II) chloride

M_n = molar concentration of tin(II) chloride after the n^{th} addition of tin(II) chloride

The average slope of the tin(II) chloride standard plot was $(8.47 \pm 0.37) \times 10^3 \frac{\mu A \cdot \text{litre}}{\text{mole}}$.

Discussion

With a half-wave potential at -0.51V vs. S.C.E. the wave due to tin(II) could be observed simultaneously with the maximum due to platinum(IV) without significant interference. Another factor which contributed significantly to this ability to observe independent waves was the difference in sensitivity of the polarographic technique in detecting tin(II) and platinum(IV) with similar concentrations. The detection of platinum(IV) using the diffusion current maximum around -0.75V was one hundred times more sensitive a measure of the presence of platinum(IV) than the diffusion current at -0.51V was a measure of the presence of tin(II). This meant that for the reduction

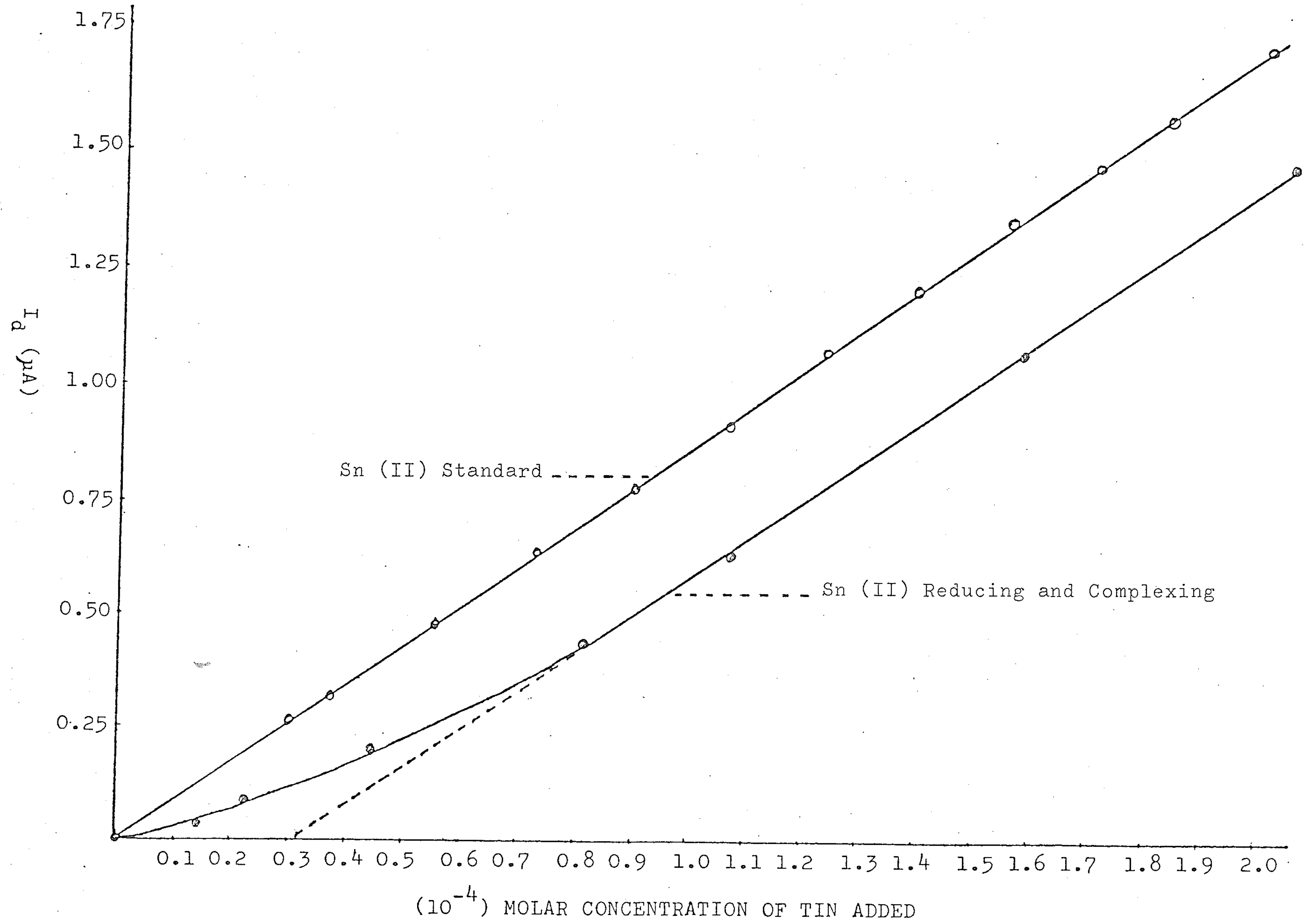
$$\text{Pt(IV)} + \text{Sn(II)} \longrightarrow \text{Pt(II)} + \text{Sn(IV)}$$

even if some tin(II) is present before all the platinum is reduced the contribution to the diffusion current by the tin(II) is insignificant when compared to the diffusion current for the platinum (IV) and can be ignored when determining platinum(IV).

Two other problems had to be considered. They involved

Figure 14

Diffusion Current (I_d) versus Molar Concentration
of Tin (II) Chloride Added
for the Tin (II) Standard and the Tin (II) Used
in Reducing and Complexing Platinum


1.75
1.50
1.25
1.00
0.75
0.50
0.25
I_d (μA)
Sn (II) Standard
Sn (II) Reducing and Complexing
0.1 0.2 0.3 0.4 0.5 0.6 0.7 0.8 0.9 1.0 1.1 1.2 1.3 1.4 1.5 1.6 1.7 1.8 1.9 2.0
(10^{-4}) MOLAR CONCENTRATION OF TIN ADDED

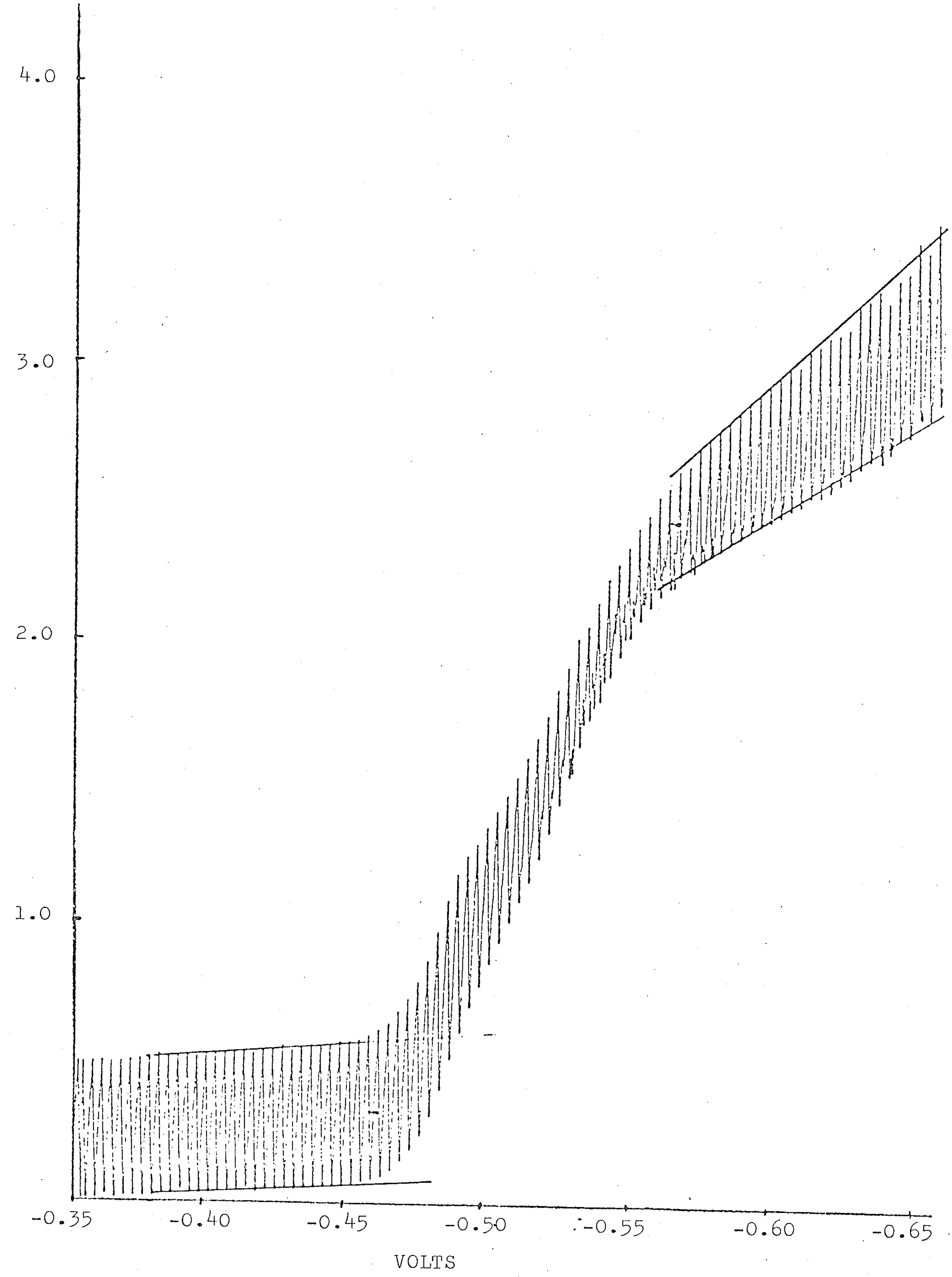
the polarographic behaviour of platinum(II) and tin (IV).

It was not possible to test platinum (II) in the chosen medium because, as has been shown earlier, the perchloric acid caused immediate and complete oxidation to platinum(IV). Kivalo and Laitinen[26] however state that the platinum (II) maximum is half the height of platinum (IV) and since the free platinum (II) concentration in the chosen medium should never be very large the polarographic reduction of platinum(II) should never be significant compared to that of platinum (IV).

Tests with tin(IV) showed no polarographic wave in the region of study, but equimolar additions of tin (IV) to tin (II) samples caused an increase in the slope of the diffusion current plateau for the tin (II) wave (fig 15). Measurement of the diffusion current at the half-wave potential showed that the tin (IV) had no significant effect on the diffusion current due to tin (II).

Figure 15

Polarographic Wave for Tin(II) Chloride (1.86×10^{-4} M)
with Equimolar Tin(IV) Chloride


4.0
3.0
2.0
1.0
I_d (μA)
-0.35
-0.40
-0.45
-0.50
-0.55
-0.60
-0.65
VOLTS

E. Polarographic Study of the Oxidation State of Platinum in the Complex

Preliminary titrations of platinum(IV) with the tin(II) chloride solution showed that as the amount of tin(II) increased, the maximum attributed to the platinum(IV) shifted from -0.75V to -0.68V (fig 16). Most amperometric titrations involve measuring the change in current at a fixed potential, however since no potential could be chosen as being representative of the platinum (IV) maximum, a scan of the full maximum was necessary to detect the presence of platinum (IV).

It was also noted in preliminary studies that the half-wave potential for the reduction of tin(II) shifted from -0.51V in the standard to -0.46V in the presence of platinum (fig 16).

Experimental

10.0 ml of dilute platinum(IV) stock solution were prepared using the modified method of Berman and Goodhue[1] described earlier and 20.0 ml of solution 0.5 M sodium chloride and 2.0 M perchloric acid were added. The 45.0 ml of solution contained 1.49×10^{-6} moles of platinum.

Tin(II) chloride was prepared by dissolving mossy tin as described earlier and standardized iodometrically.

The tin(II) chloride was added to the polarographic cell containing the platinum by burette. Deaeration was done as described above, drop time for the dropping mercury electrode was three seconds per drop and 5 drops of 0.1% Triton X suppressor were used.

Results

The results are shown in table VIII and the polarographic scans illustrated in figure 16. Figure 16 shows the diffusion current for tin (II) after each addition of tin (II) chloride measured at a half wave potential of -0.46V with a sensitivity of 0.02 µA/mm. The polarographic maxima for platinum (IV) are shown at a sensitivity of 1.0 µA/mm. It can be seen from figure 16 that after the fourth addition of tin (II) chloride (giving a tin-platinum ratio of 1.36/1) the maximum due to platinum (IV) is no longer evident. The values shown in table VIII for I_d (Sn (II)) were plotted against the corrected concentration for tin (II) chloride added and are shown in figure 14. The slope of the curve was determined at each point as in:

$$\text{(E)} \qquad X = \frac{\sum_{i=1}^{a-n} \left(\frac{C_{n+i} - C_n}{M_{n+i} - M_n} \right)}{(a - n)}$$

and the value of X compared to $\overline{X}$ of equation (D). It was found that before a 2/1, tin to platinum molar ratio was achieved the diffusion current did not respond linearly to increased molar tin concentration, but that beyond the 2/1 tin to platinum ratio the slope of the plot was not significantly different from $\overline{X}$. Extrapolation of the linear portion of the graph to $I_d = 0.0$ (fig 14) showed that the tin(II) response was shifted by 1.49×10^{-6} moles of tin(II). This corresponded exactly to a 1/1, tin to platinum molar ratio.

Discussion

The results clearly show that the reduction of platinum (IV) by tin(II) chloride is a 1/1 process in tin and platinum and the reduction before complexation is:

$$\mathrm{Pt(IV)} + \mathrm{Sn(II)} \longrightarrow \mathrm{Pt(II)} + \mathrm{Sn(IV)}$$

The lack of linear response of I_d (Sn(II)) to tin(II) chloride added until a tin to platinum molar ratio of approximately 2/1 suggested a competitive reaction to the reduction, involving the formation of a 1/1 complex of tin(II) and platinum (II). Since the concentration of free tin(II) would be zero until the reduction of platinum(IV) was complete the polarographic wave at -0.46V was assigned to complexed tin(II) as has since been done by Elizarova and Matvienko[9]. This 1/1 complex must have a relatively large equilibrium constant since any tin (II) which dissociated would immediately be used in the reduction of platinum (IV). If the 1/1 complex dissociated to any great extent the plot of I_d (Sn(II)) vs. $[\mathrm{Sn(II)}]$ (added) in the presence of platinum(IV) shown in figure 14 would have simply followed the extrapolated line.

These results would seem to make the spectrophotometric work reported earlier seem rather suspect since no absorption due to the complex was observed until tin to platinum molar ratios exceeded 2.5/1. However, at tin to platinum ratios of less than 2/1 formation of the 1/1 complex is incomplete, thus keeping its concentration low. It can also be seen from tables IV, V and VI that full colour development for the complex, whose absorption is measured at 254, 273, 310 and 403 nm, required tin to platinum ratios greater than 30/1.

These considerations suggested the fairly rapid formation of a stable 1/1 complex with low molar absorptivity followed by a less favoured reaction requiring large excesses of tin(II) chloride to drive the equilibrium to products. These products would most likely involve a complex or complexes of tin and platinum having molar ratios greater than 1/1 and absorption maxima in the electronic spectrum at the wavelengths most commonly associated with the platinum - tin(II) chloride complex or complexes (254 nm, 273 nm, 310 nm and 403 nm).

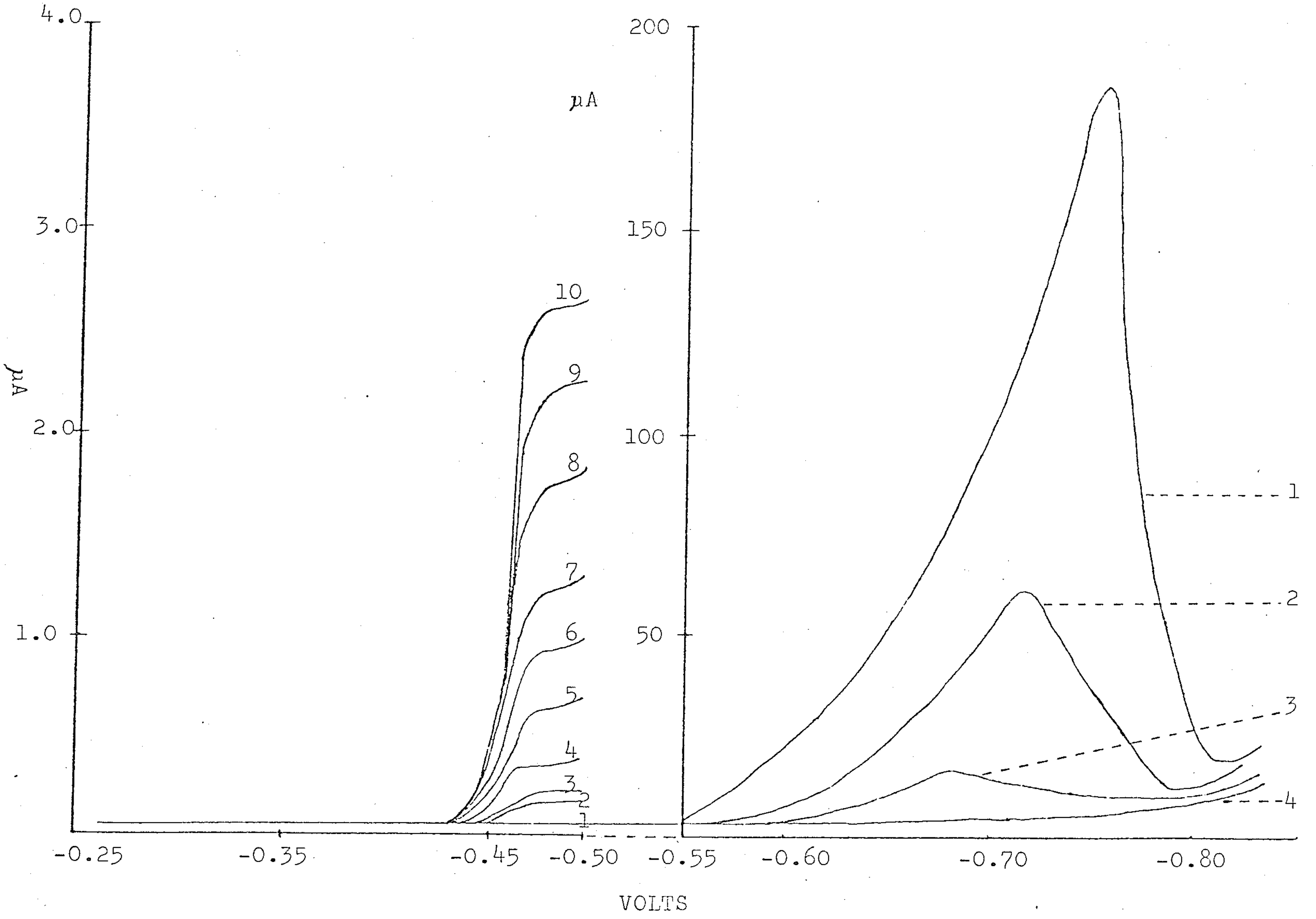
Table VIII - AMPEROMETRIC TITRATION OF PLATINUM* (IV) WITH SIMULTANEOUS DETERMINATION OF TIN (II)

TRIAL	ml $SnCl_2$ ADDED	MOLAR CONCENTRATION Sn II	Sn/Pt MOLAR RATIO	I_d (Sn (II)) µA	I_d (Pt) µA
1	0.00	0	0.0	0.000	180
2	0.25	1.40×10^{-5}	0.43/1	0.029	56.2
3	0.40	2.23×10^{-5}	0.68/1	0.088	14.7
4	0.80	4.42×10^{-5}	1.36/1	0.216	
5	1.50	8.16×10^{-5}	2.55/1	0.440	
6	2.00	1.08×10^{-4}	3.40/1	0.632	
7	3.00	1.58×10^{-4}	5.10/1	1.06	
8	4.00	2.07×10^{-4}	6.80/1	1.47	
9	5.00	2.53×10^{-4}	8.50/1	1.84	
10	6.00	2.98×10^{-4}	10.20/1	2.24	

*The sample contained 1.49×10^{-6} moles of platinum (IV) in an initial volume of 45.0 ml

Figure 16

Amperometric Titration of Platinum (IV) with Simultaneous Determination of Tin (II). Sample contained 1.49 x 10^{-6} moles of platinum (IV) and the trials 1-10 indicate the successive additions of tin (II) chloride as listed in table VIII.


4.0
3.0
2.0
1.0
µA
µA
10
9
8
7
6
5
4
3
2
1
200
150
100
50
1
2
3
4
-0.25
-0.35
-0.45
-0.50
-0.55
-0.60
-0.70
-0.80
VOLTS

VII. Additional Spectrophotometric Studies

Since the previous studies suggested the formation of a complex 1/1 in tin and platinum with a low molar absorptivity it appeared that the absorption at wave-lengths 310 nm and 403 nm must be due to a complex or complexes of higher tin to platinum ratios. The absorbances at 310 and 403 nm were chosen for study since they are in a region of the electronic spectrum in which absorbance due to tin(II)chloride is zero for preparation of the complex by the method of Berman and Goodhue. These maxima are those most commonly chosen for quantitative work involving the coloured platinum - tin(II)complex.

The limited range of adherence to Beer's Law, the dual reducing and complexing role of the tin(II)chloride and the high probability of formation of two or more complexes made attempts at studies by continuous variations[27] and equivalent solutions[28] completely unproductive. Plots of ε vs. $[Sn(II)]$ as in the work of Baldwin and Stanks[28] for platinum concentrations ranging from 2.32 ppm to 11.6 ppm showed no significant difference for plots for 2.32 ppm and 11.6 ppm platinum. The most significant information gained from these plots was that the absorbance showed an extremely erratic behaviour at 310 and 403 nm when the tin to platinum ratio was greater than 5/1 but less than that required for full colour development, approximately 50/1. This erratic absorbance behaviour lead to a qualitative stability study of the complex or complexes associated with absorption at 310 and 403 nm.

Experimental

Eight platinum solutions 6.96 ppm platinum (IV) were prepared by the modified method of Berman and Goodhue and tin(II) chloride solution was prepared by the process of dissolving mossy tin described above. The tin(II) chloride solution was standardized iodometrically as 6.36 x 10^{-3} M and maintained under a nitrogen atmosphere. At the end of the study the concentration of tin(II) chloride was again determined iodometrically and found to be 6.32 x 10^{-3} M. This decrease in tin(II) chloride concentration (0.6%) was not considered to be significant in terms of the study. The tin(II) chloride solution was added in different amounts to each platinum solution and after mixing and dilution to the mark with water the absorbance of the complex was measured at 310 and 403 nm at regularly spaced time intervals for a period of fifteen minutes. All measurements were made against a reagent blank which had been prepared simultaneously with the sample.

Results

The results are summarized in tables IX and X and a plot of the data in table IX is shown in figure 17.

The results of this study show that the absorbance at 310 nm and 403 nm mirror each other in every respect with the absorbance at 403 nm being about 25% of that at 310 nm. This behaviour strongly suggests that the absorption at 310 nm and

403 nm in the electronic spectrum are associated with the same complex. The reason for the erratic results in the ε vs. $[\text{Sn(II)}]$ plots of the equivalent solutions work also becomes apparent. At intermediate tin to platinum molar ratios the absorption at 310 nm and 403 nm can be seen to rise to a maximum after ten minutes and then start to decrease. For platinum samples containing 23.2 ppm platinum this same behaviour was observed at tin to platinum molar ratios of 5/1.

A comparison with the results of table III for 6.96 ppm platinum shows that at tin to platinum molar ratios of 20/1 colour development of the complex which absorbs at 310 nm and 403 nm is only 93% after eleven minutes and at tin to platinum molar ratios of approximately 30/1 colour development is 94% after five minutes.

It can also be seen that at low and high tin to platinum molar ratios (less than 5/1 and greater than 15/1) colour development builds to a maximum and then remains relatively constant.

Table IX - VARIATION OF COMPLEX ABSORPTION AT 310 nm FOR A CONSTANT PLATINUM* CONCENTRATION WITH VARYING TIN(II) CHLORIDE CONCENTRATION

TIME	MOLAR RATIOS - TIN: PLATINUM							
MINUTES	3.6/1	7.1/1	10.7/1	14.2/1	17.8/1	21.3/1	24.9/1	28.4/1
1.0	0.050	0.120	0.315	0.385	0.461	0.860	0.860	0.850
3.0	0.038	0.189	0.495	0.620	0.780	0.890	0.960	0.980
5.0	0.040	0.241	0.575	0.730	0.890	0.960	1.00	1.01
7.0	0.037	0.275	0.621	0.735	0.920	0.980	1.02	1.03
9.0	0.037	0.292	0.631	0.680	0.930	0.980	1.02	1.04
11.0	0.039	0.303	0.600	0.625	0.930	1.00	1.03	1.05
13.0	0.038	0.301	0.523	0.592	0.940	1.00	1.04	1.05

*Platinum concentration = 6.96 ppm

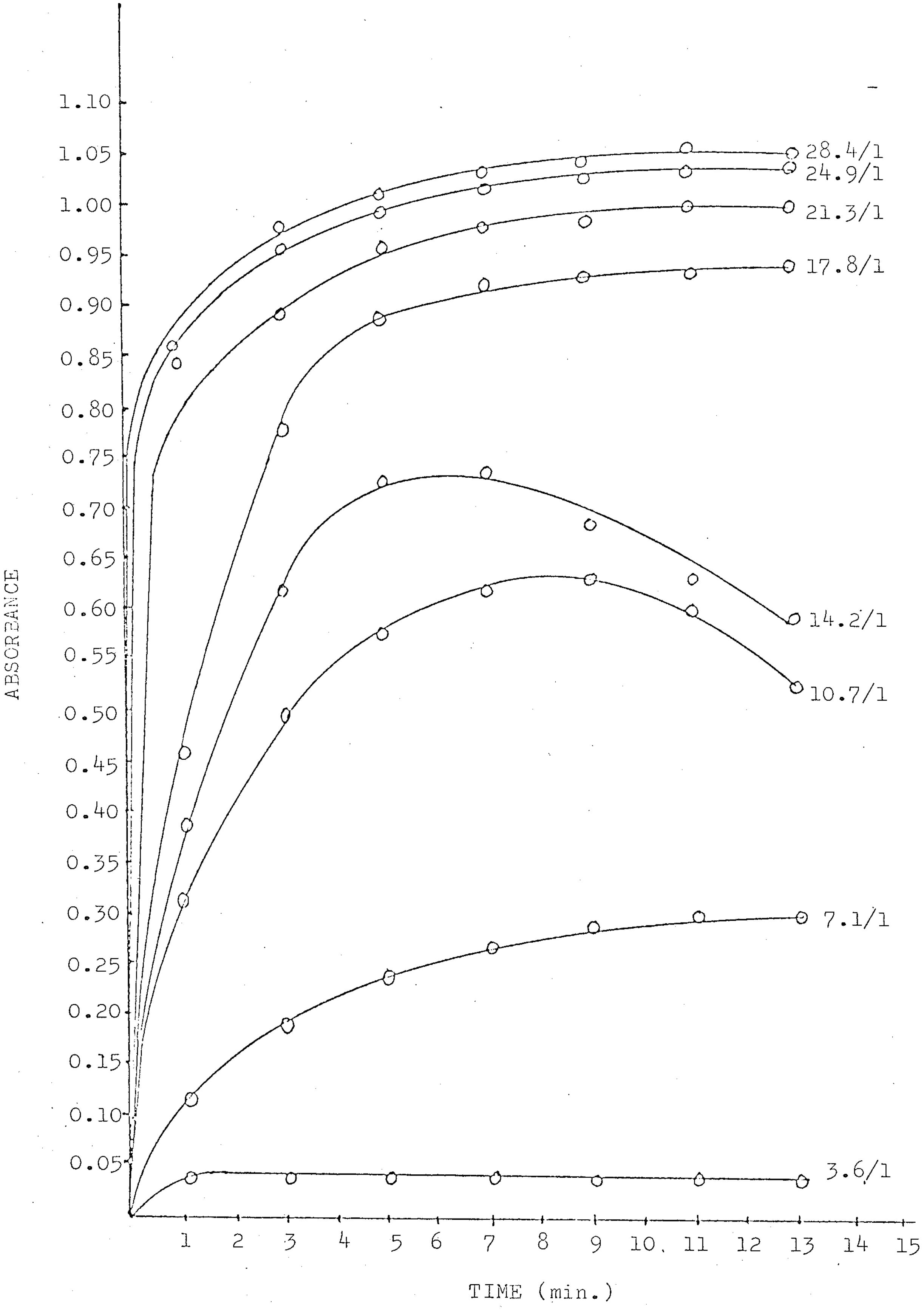
Table X - VARIATION OF COMPLEX ABSORPTION AT 403 nm FOR A CONSTANT PLATINUM* CONCENTRATION WITH VARYING TIN(II) CHLORIDE CONCENTRATION

TIME	MOLAR RATIOS - TIN: PLATINUM							
MINUTES	3.6/1	7.1/1	10.7/1	14.2/1	17.8/1	21.3/1	24.9/1	28.4/1
2.0	0.013	0.042	0.108	0.138	0.165	0.205	0.225	0.245
4.0	0.017	0.052	0.136	0.174	0.215	0.235	0.252	0.257
6.0	0.020	0.060	0.154	0.187	0.231	0.248	0.258	0.268
8.0	0.018	0.070	0.156	0.176	0.235	0.251	0.262	0.273
10.0	0.018	0.072	0.156	0.153	0.238	0.255	0.269	0.272
12.0	0.018	0.075	0.143	0.147	0.238	0.262	0.268	0.272
14.0	0.018	0.073	0.135	0.140	0.237	0.258	0.268	0.271

*Platinum concentration = 6.96 ppm

Figure 17

Absorbance vs Time for a Constant Platinum Concentration with Varying Tin(II) Chloride Concentration Measured at 310 nm


ABSORBANCE
1.10
1.05
1.00
0.95
0.90
0.85
0.80
0.75
0.70
0.65
0.60
0.55
0.50
0.45
0.40
0.35
0.30
0.25
0.20
0.15
0.10
0.05
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
TIME (min.)
28.4/1
24.9/1
21.3/1
17.8/1
14.2/1
10.7/1
7.1/1
3.6/1

Discussion

The results of this final spectrophotometric study clearly illustrate some of the difficulties involved in a study of the platinum - tin(II) chloride complex which absorbs in the electronic spectrum at 310 nm and 403 nm. The decrease in absorbance at intermediate tin to platinum molar ratios with time which caused difficulties in continuous variations and equivalent solutions studies and has been attributed to complex instability by earlier authors[3,4] is not inconsistent with the findings of Young *et al*[15]. These authors suggested that there are two isomers of a complex involving the $[PtCl_2(SnCl_3)_2]^{-2}$ anion, however no conclusive evidence for the existence of this anion has been obtained in the present study. The decrease in absorbance at intermediate tin to platinum molar ratios with time can be explained in terms of these suggested isomers as initial formation of a favoured trans complex which at intermediate tin to platinum concentrations is in equilibrium with a cis complex. At higher tin to platinum ratios the excess of tin(II) chloride suppresses this rearrangement by shifting the equilibrium in favour of the trans complex. If Young's[15] suggestion concerning isomers is correct the absorption at 310 nm and 403 nm are associated with the trans complex and the decrease in absorbance with time reflects the rearrangement to a cis complex. Unfortunately an added complication arises since, according to Young, the cis isomer also absorbs at 310 nm to a small extent.

The present study has also shown that the total tin and platinum concentration has a marked effect in determining the tin to platinum ratios at which various spectral absorptions and phenomenon occur. Absorption at 273 nm appears at lower tin to platinum molar ratios as the total tin and platinum concentration increases. Decrease in absorbance with time appears at tin to platinum ratios of 15/1 for 6.96 ppm platinum but only 5/1 for 23.2 ppm platinum. These trends seem to suggest a possible kinetic effect but as has been shown in the present work these effects are rather difficult to study quantitatively using spectrophotometric techniques. At platinum concentrations exceeding 6.0 ppm absorption at 310 nm is non-linear and absorption at 403 nm, a much less sensitive measure of complex concentration, is non-linear at platinum concentrations exceeding 25 ppm.[4]

This final spectrophotometric study does however indicate the direction future studies of the platinum - tin(II)chloride complex might take.

VIII. Conclusions

The spectrophotometric studies clearly established, that in a perchloric acid medium, platinum exists in an oxidation state of four and that addition of tin(II) chloride causes reduction at least to platinum(II) and possibly to platinum (0).

The polarographic work showed that reduction of platinum (IV) by tin(II) chloride proceeds only as far as platinum(II) and these studies also suggested initial formation of a complex 1/1 in tin and platinum. It was concluded that this 1/1 complex which required a 2/1 tin to platinum molar ratio in order to form, must have a low molar absorptivity since no absorption in the spectrophotometric studies was observed below a tin to platinum molar ratio of 2/1 except that attributed to platinum(IV) and platinum(II).

The absorbances measured at 254 nm, 273 nm, 310 nm and 403 nm must therefore be due to a complex or complexes with tin to platinum molar ratios greater than 1/1. The final spectrophotometric study leads to the conclusion that an equilibrium exists involving at least two complexes at tin to platinum molar ratios greater than 1/1. This equilibrium involves initial formation of one complex at low tin to platinum ratios, formation of the same complex at intermediate tin to platinum ratios followed by rearrangement or dissociation, and at high tin to platinum ratios, formation of one complex with rearrangement suppressed by a large excess of tin(II) chloride.

Essentially full complexation is achieved at tin to platinum ratios of 50/1 and complexation is 97% complete after ten minutes at ratios of approximately 30/1 for the first complex formed which absorbs at 310 nm and 403 nm.

In view of these conclusions it can be seen that the results of Elizarova and Matvienko,[8,9] which were published after completion of this study, were in error in one aspect. They failed to consider the oxidation of platinum(II) to platinum(IV) by perchloric acid. Considering their method of study it can be seen that they would have also suggested a complex of platinum (II) as does the present study had they only recognized this oxidation by perchloric acid.

The present study has certainly not exhausted the possible studies that can be done on the complexes of platinum and tin(II) chloride. In fact a large part of the work has pointed out the limitations of an oversimplified approach to the problem and the need for some very highly controlled studies.

A technique which might prove fruitful would be to determine the length of time required for maximum colour development for the complex absorbing at 310 and 403 nm for different tin to platinum ratios. If at the point of maximum colour development the complex can be quantitatively extracted by high molecular weight amines as suggested by Khattak and Magee[17] with a five-fold increase in sensitivity for the absorption at 403 nm, ligand number and stability constant might be obtainable by a method of equivalent solutions. This study would not be done in a perchloric acid medium as were all studies in the present work however, and care would have to be taken to assure that the same complex is present in the organic phase as was present in the aqueous phase.

The main efforts in further study of the platinum - tin (II) chloride complex should be in the search for a technique or aqueous medium in which platinum(IV), platinum(II), tin(IV) and tin(II) can be detected simultaneously in the same medium with no interference between the ions.

The present work produced a new medium for the polarographic study of tin(II) chloride with insignificant interference from tin(IV) which also allowed measurements of platinum(IV) concentrations, however the medium and technique fell short in the detection of free or complexed platinum(II) and free tin(IV).

IX. Bibliography

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