THE EFFECT OF STANNOUS CHLORIDE ON THE SOLVENT EXTRACTION OF THE TETRACHLOROPLATINATE(II) ION BY TRIPHENYLPHOSPHINE

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by

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ABSTRACT

The effect of $SnCl_2$ on the solvent extraction of K_2PtCl_4 in HCl into CH_2Cl_2 using triphenylphosphine (PPh_3) has been studied in detail. It has been found that $SnCl_2$ dramatically increases the rate and efficiency of extraction. Our studies show that the percentage Pt extraction depends upon the time allowed for extraction, the Pt(II)/PPh_3 ratio, the Pt(II)/Sn(II) ratio and the HCl concentration in a complicated way.

The influence of $SnCl_2$ on the extraction has been ascribed to a 'labilizing effect'. Our results show however that tin is initially extracted into the organic phase and evidence exists for the formation of $Pt(SnCl_3)Cl(PPh_3)_2$ in this phase. Tin is back-extracted into the aqueous phase over time indicating the disproportionation

$$[Pt(SnCl_3)Cl(PPh_3)_2]_{(org)} \rightleftarrows [PtCl_2(PPh_3)_2]_{(org)} + SnCl_{3(aq)}^-$$

CONTENTS

CHAPTER 1

CHAPTER I

1. INTRODUCTION

The interaction of stannous chloride with the noble metals, in particular platinum, has been known for over a century [1,2]. The characteristic red-orange colour of the complexes so produced has been used in trace analysis of the platinum group metals. Such systems are also known to possess interesting catalytic properties. Although many workers have investigated the reaction of stannous halides with the platinum metals, little detailed information about the nature of these complexes in solution is available.

1.1 The Red Platinum-Tin Species

The reaction of tin(II) chloride with platinum was first reported by Wöhler [3] who found that platinum(IV) in hydrochloric acid solution, when treated with stannous chloride gave a deep red colour that was extractable into ether.

Wöhler and Spengel [4] considered the red colour to be due to colloidal platinum, analogous to the "purple of Cassius" formed when gold chloride is similarly treated. Ayres and Meyer [5] disproved this postulate by observing that the coloured material readily passed through semi-permeable membranes and could be rapidly extracted into organic solvents.

The colour was also attributed to "chloroplatinous acid", presumably a compound of the form H_2PtCl_4 [6,7]. Ayres and Meyer [5] however concluded that the red colour in some way involved tin and was not due simply to this so-called chloroplatinous acid.

Stannous chloride has been used as a colourimetric reagent for the quantitative determination of small amounts of platinum [8-12]. The absorbance was found to obey Beer's Law up to a platinum concentration of about 30 p.p.m. The colour intensity was reported to depend on hydrochloric acid concentration, reaching a maximum at about 0,3 M (twice as strong as in 2 M acid) and was found to be more stable at higher acidities (greater than 0,7 M). The colour intensity was not affected by the stannous chloride concentration but in the presence of stannic chloride at low acidities it was found to increase. Although this procedure has been used, rapid fading of solutions, shifts of absorption peaks at various conditions and interferences by cations and anions, indicate that this is not an entirely satisfactory quantitative method.

The spectrophotometric determinations of other platinum group metals, for example rhodium and palladium, using tin(II) have also been reported [13-15].

In a detailed study on the interaction between platinum(II) and tin(II) chlorides, Ayres and Meyer [16] proposed the existence of complexes in the aqueous medium of tin to platinum ratios of 1:4, 1:2, 1:1, 3:2, 2:1, 3:1 and 5:1, with the principal product corresponding to a 5:1 ratio. It was suggested that one mole of tin(II) was oxidised to tin(IV) simultaneously with reduction of platinum(II) to platinum(0), yielding a cationic product containing four moles of tin(II) and four moles of chloride associated with one platinum, $[PtSn_4Cl_4]^{4+}$. The platinum was thought to exist in zero oxidation state, analogous to the zero-valent metal in tetracyanonickelate and -palladate [17,18].

Subsequent investigations of the reaction of platinum, ruthenium, rhodium and iridium with tin(II) chloride in aqueous acid solution suggested that these coloured complexes are anionic [19].

Amongst the complexes which Young and coworkers [19] isolated from these solutions were the proposed *cis*- and *trans*-isomers of $[PtCl_2(SnCl_3)_2]^{2-}$. They suggested that the trichlorostannate(II) ion is a donor ligand using its lone-pair electrons so that the usual common formal oxidation state and stereochemistry of the platinum can be preserved.

The proposed square-planar *cis*- and *trans*- forms of $[Pt(Cl_2(SnCl_3)_2]^{2-}$ were isolated as the tetramethylammonium salts, one of which is red and the other yellow. Young *et al* found both forms to exist in solutions at Sn:Pt ratios of 2:1 but at higher concentrations of tin, precipitation with tetramethylammonium chloride gave red salts which appeared to contain higher ratios up to 5:1. This led to the proposal that tin was coordinated to platinum to give a quinquecoordinate ion, $[Pt(SnCl_3)_5]^{3-}$. Analyses of samples obtained corresponded with this stoichiometry. A determination of the configuration of the $[Pt(SnCl_3)_5]^{3-}$ anion by x-ray diffraction showed the ion to be a trigonal bipyramid consisting of a central platinum atom surrounded by five $SnCl_3^-$ ligands attached through platinum-tin bonds [20].

Young and coworkers [19] proposed that several independent equilibria exist simultaneously in solutions containing tin(II) chloride and platinum(II) chloride:

$SnCl_2 + Cl^- \rightleftarrows SnCl_3^-$
$[PtCl_4]^{2-} + SnCl_3^- \rightleftarrows [PtCl_3(SnCl_3)]^{2-} + Cl^-$
$[PtCl_3(SnCl_3)]^{2-} + SnCl_3^- \rightleftarrows$ *trans*-$[PtCl_2(SnCl_3)_2]^{2-} + Cl^-$
trans-$[PtCl_2(SnCl_3)_2]^{2-} \rightleftarrows$ *cis*-$[PtCl_2(SnCl_3)_2]^{2-}$
cis- and *trans*-$[PtCl_2(SnCl_3)_2]^{2-} + 3SnCl_3^- \rightleftarrows [Pt(SnCl_3)_5]^{3-} + 2Cl^-$

Young considered the yellow form of $[PtCl_2(SnCl_3)_2]^{2-}$ to be the *cis*-isomer due to its greater thermodynamic stability and solubility in polar solvents compared with the red complex. However, the existence of the latter has in fact been questioned in a Mössbauer study reporting that this red compound in fact yields the same spectrum as the red pentakis anion $[Pt(SnCl_3)_5]^{3-}$ [21].

A very recent multinuclear NMR study has also questioned the existence of the yellow and red forms of $[PtCl_2(SnCl_3)_2]^{2-}$ [22]. Red solutions of the supposed red isomer isolated from 3 M HCl appeared to be a mixture of red $[Pt(SnCl_3)_5]^{3-}$ and the yellow $[PtCl_2(SnCl_3)_2]^{2-}$. The magnitude of $J(^{195}Pt, {}^{119}Sn)$ in these anions, as with other square planar complexes involving Pt(II) and $SnCl_3^-$ [23], was found to be unusually large. Values of $^1J(^{195}Pt, {}^{119}Sn)$ for $[Pt(SnCl_3)_5]^{3-}$ and yellow $[PtCl_2(SnCl_3)_2]^{2-}$ in acetone-d_6 are 16 024 and 27 640 Hz respectively [22].

Other workers have also found that the red platinum-tin species is anionic [24-27]. Khattak and Magee [27] found the red complex to be readily extractable into organic solvents using high molecular weight amines. They concluded that the complex must be anionic in nature and that liquid anion exchange occurs between the charged complex and the high molecular weight amine in the following way:

$$RNH_{2(org)} + H^+A^-_{(aq)} \rightleftarrows [RNH_3{}^+A^-]_{(org)}$$

$$n[RNH_3{}^+A^-]_{(org)} + [MX]^{n-}_{(aq)} \rightleftarrows ([RNH_3{}^+]_n[MX]^{n-})_{(org)} + nA^-_{(aq)}$$

where $H^+A^-_{(aq)}$ represents hydrochloric acid and $[MX]^{n-}_{(aq)}$ the platinum-tin complex.

Recently however, Russian workers have again suggested, from their potentiometric and polarographic studies, that on reaction with tin(II) chloride in hydrochloric acid medium, platinum(II) is reduced to the zero-valent state [28]. These results appear to be in direct contrast with an overwhelming body of evidence that the Pt(II) is not necessarily reduced to Pt(0) in aqueous acid solution by $SnCl_2$.

Complexes of platinum and stannous halides have also been found to possess some remarkable homogeneous catalytic properties.

Schwager and Knifton [29] reported the use of $PtCl_2(PPh_3)_2$-$SnCl_2$ as a catalyst for the homogeneous hydroformylation of olefins to aldehydes. A similar catalytic system has been used by other workers to effect the isomerisation of 1,5-cyclooctadiene [30]. Tin(II) chloride, essential for the isomerisation, was thought to activate the platinum catalyst by coordination through the $SnCl_3{}^-$ ligand which is believed to be a strong π-acceptor and a weak σ-donor. Ligand stabilised platinum(II) - Group IVA metal halide complexes, for example $[(C_6H_5O)_3P]_2PtCl_2$-$SnCl_2$, have also been found to catalyse the homogeneous carbonylation of α-olefins to carboxylic acids and esters [31].

It thus appears that although the platinum-tin system has been widely studied, the exact nature of the red species formed in solution is not fully understood. Researchers have suggested the red colour to be due to "colloidal platinum", "chloroplatinous acid", a tetra-positive cationic species and anionic platinum-tin complexes, with various oxidation states for the two metals. A number of equilibria are thought to exist in the solutions although stability constants for such processes are not known.

In conclusion it may be said that the red colour of such solutions is due to the formation of anionic platinum-tin complexes. Evidence from NMR [22] and x-ray crystallographic [20] studies has confirmed the existence of direct bonding of the $SnCl_3^-$ ligand to the platinum and it is likely that both metals are in the divalent oxidation state. From NMR [22] and Mössbauer [21] data it is evident that at least the complexes $[PtCl_2(SnCl_3)_2]^{2-}$ and $[Pt(SnCl_3)_5]^{3-}$ are the species giving the red colour to solutions of platinum and tin.

1.2 The Solvent Extraction of Platinum

Due to the increased demands for platinum group metals, in particular platinum, in recent years, much interest has been centred on the efficient recovery and separation of these elements [32].

A recent paper by researchers at Matthey Rustenburg Refiners (UK) Ltd. describes the application of solvent extraction to platinum group metals refining [33]. Their process involving dissolution, precipitation and distillation methods was found to be inefficient due to incomplete separation at various stages and contamination of the precipitates. Since it was felt that a solvent extraction based process could achieve a cleaner separation, higher product purities and more rapid overall processing, work was started in the 1970's in the Johnson Matthey Group Research Laboratories to develop such a process. It appears however that industrial research in this field is generally of a confidential nature and exact details of the separation methods used are not reported in the literature.

Many independent workers have undertaken research on the extractive concentration of platinum-group elements using a variety of solvents. The use of high molecular weight amines as extractants was first reported by Smith and Page [34]. Reagents such as N,N-dioctylacetamide [35], 2-mercaptobenzothiazole [36], di-n-octylsulphide [37] and 2-octylaminopyridine [38] have also been used.

The ease with which platinum-stannous chloride complexes may be extracted into organic phases has been recognised as an extremely useful property. It provides a good method for separating and preconcentrating the noble metals from other base metals that do not interact significantly with stannous chloride.

Ayres and Meyer [5] found that the red platinum-tin colour was extracted almost quantitatively into amyl and ethyl acetate. They found however that the colour of the extract faded rapidly but could be stabilised for at least an hour by addition of 1 % resorcinol. Almost all the platinum group metals were found to form similarly coloured products, extractable into the organic phase.

The complexes formed on mixing platinum(IV) and tin(II) solutions were found to be quantitatively extracted into an organic phase of chloroform or benzene containing long-chain high molecular weight amines [27]. Comparison of the absorption spectra of the coloured species in the aqueous and amine phases indicated the presence of the same species in each medium.

A number of studies on the solvent extraction of platinum metals in the presence of $SnCl_2$ have been reported by Russian workers. Solvents such as sulfoxides [39] and thioureas [40] have been used as suitable extractants for the platinum group metals. Gorbanev *et al* [41] carried out a study on the extraction of platinum metals in the presence of tin dichloride from aqueous acid solutions with tributyl phosphate and a number of other oxygen-containing solvents, such as ketones, ethers and acetates. The work was however not reported in great detail.

Triphenylphosphine (TPP or PPh_3) in an organic solvent such as benzene or toluene was also found to extract palladium, ruthenium, silver and gold from acidic aqueous solutions [42,43]. In view of these results, Mojski examined the extraction of the platinum metals from hydrochloric acid medium with triphenylphosphine in 1,2-dichloroethane [44]. He found that the presence of a large excess of stannous chloride resulted in marked differences in the extractability of the platinum group metals.

1.3 The Extraction of Platinum Metals with Triphenylphosphine in 1,2-Dichloroethane

Mojski [44] studied the extraction of platinum in the absence and presence of stannous chloride at varying acid concentrations. He has proposed various extraction mechanisms to account for his observations.

The extraction with triphenylphosphine solution in the absence of stannous chloride

Figure 1.1 shows the way in which the extraction of the platinum metals varies with the hydrochloric acid concentration under the conditions stated.

Two mechanisms were proposed for the extraction of platinum-metal chloride complexes with triphenylphosphine:

(a) Solvation

$$MCl_p^{(p-n)-} + mTPP_{(org)} \rightleftarrows MCl_n(TPP)_{m(org)} + (p-n)Cl^-$$

(b) Ion-exchange

$$MCl_p^{(p-n)-} + (p-n)(TPPH^+Cl^-)_{(org)} \rightleftarrows (TPPH^+)_{p-n}MCl_{p(org)}^{(p-n)-} + (p-n)Cl^-$$

where M = platinum group metal.

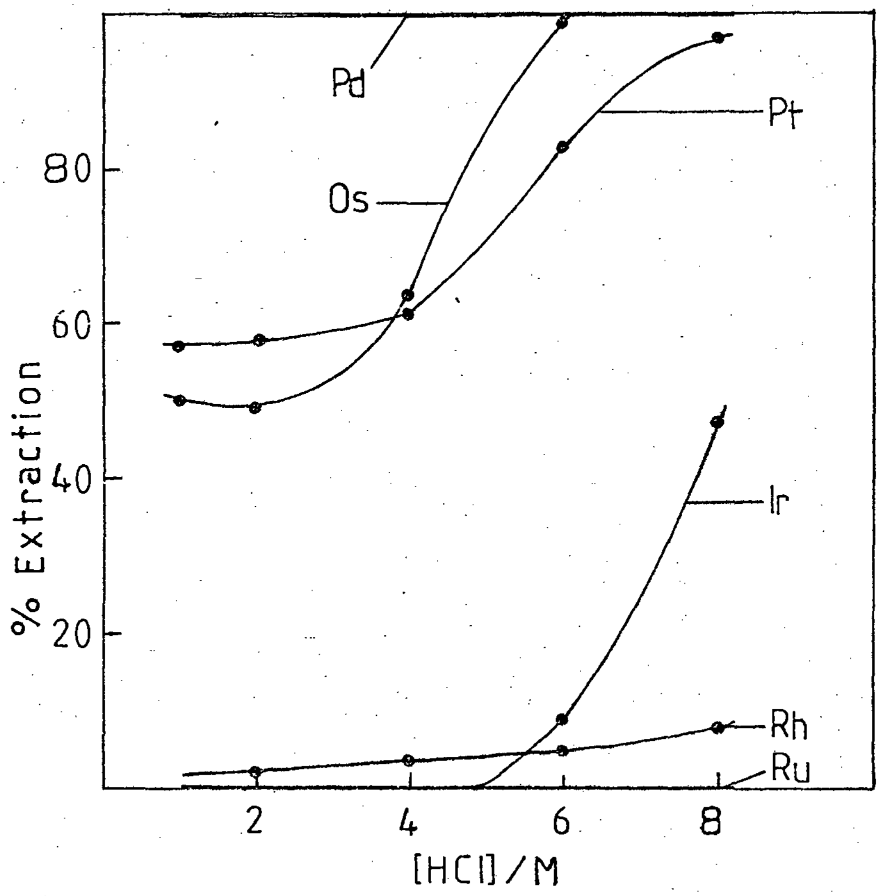


Figure 1.1 Dependence of the extraction of platinum metals (0,001 M) on acid concentration using TPP (0,1 M) in dichloroethane.

Mojski considered the solvation mechanism to predominate at low acidity and proposed that the inertness of the chloride complexes of the platinum metals, excluding palladium, resulted in their poor extraction with TPP.

In strongly acid medium, he proposed that triphenylphosphine being a weak base, forms a cation $TPPH^+$ which could participate in extraction by the ion-exchange mechanism. The increased extraction of platinum, osmium and iridium at high acidity was thought to indicate that the ion-exchange mechanism was involved under these conditions.

The extraction with triphenylphosphine solution in the presence of stannous chloride

Mojski found that, with the exception of osmium, stannous chloride dramatically increased the percentage extraction of the platinum metals. The effect of stannous chloride on the extraction was described purely as a "labilizing effect". Mojski proposed the formation of tin-containing complexes of the type $MCl_k(SnCl_3)_l^{n-(k+l)}$ in which the replacement of $SnCl_3^-$ by another ligand is not subject to such kinetic difficulties as is replacement of a chloride ligand.

Various procedures were used to study the effect of stannous chloride. The results are summarised in Figure 1.2. Mojski found, using atomic absorption spectrophotometry, that his organic extracts did not contain tin. From these results, he concluded that the stannous chloride is a labilizing agent, involved in complex formation only in the aqueous phase.

Two possible extraction mechanisms were proposed, the former of which was thought to predominate:

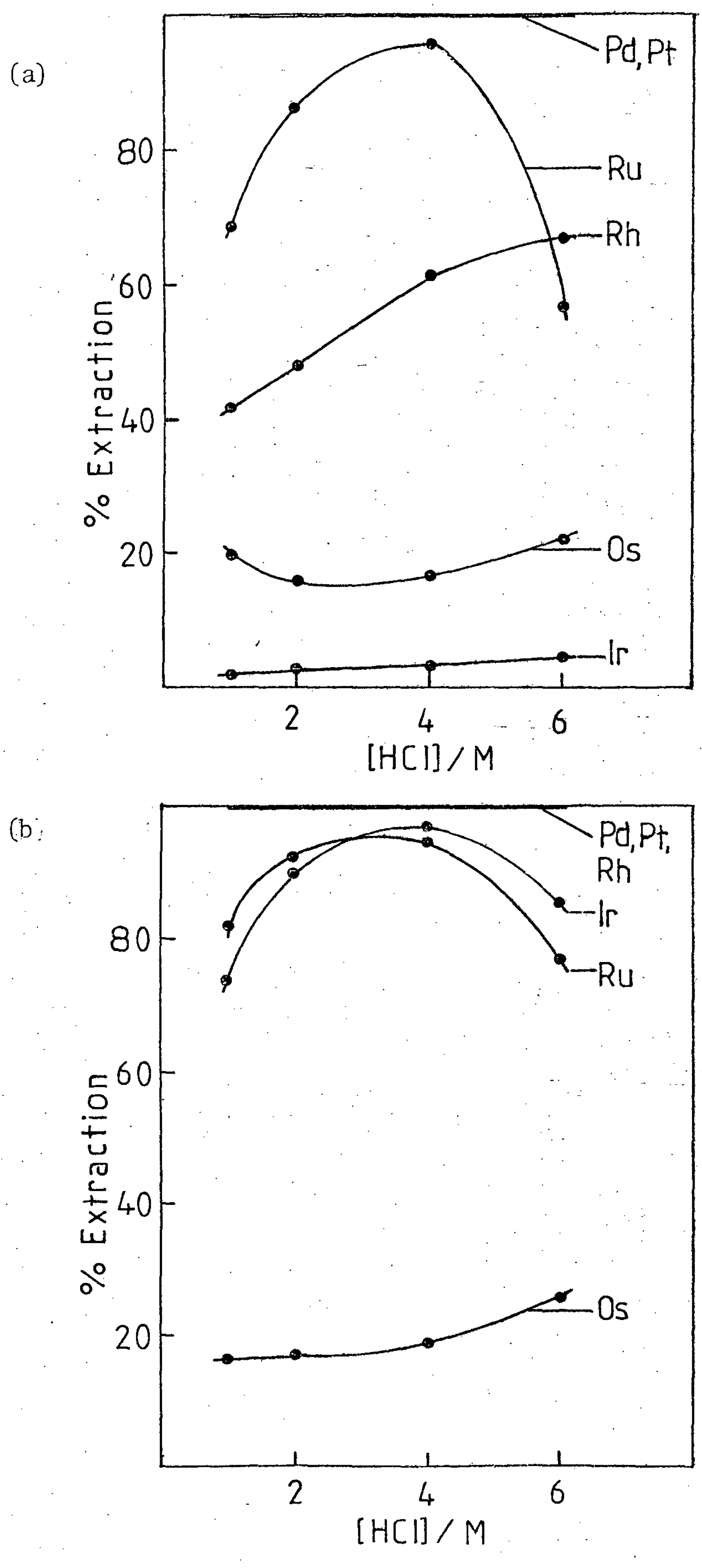


Figure 1.2 The dependence of the extraction of platinum metals (0,001 M) on acid concentration in the presence of $SnCl_2$ (0,1 M) using TPP (0,1 M) in dichloroethane (a) without heating (b) with heating before extraction.

(a) Solvation

$$MCl_k(SnCl_3)_l^{n-(k+l)} + mTPP_{(org)} + (n-k)Cl^- \rightleftarrows MCl_n(TPP)_{m(org)} + lSnCl_3^-$$

(b) Ion-exchange

$$MCl_k(SnCl_3)_l^{n-(k+l)} + lCl^- + (p-n)(TPPH^+Cl^-)_{(org)} \rightleftarrows$$
$$[MCl_p{}^{(p-n)-}(TPPH^+)_{(p-n)}]_{(org)} + lSnCl_3^- + (k+l-n)Cl^-$$

1.4 Objectives of Research

In his conclusion, Mojski [44] stated the following:

> "In the extraction of platinum metals with triphenylphosphine stannous chloride is a labilizing agent and does not enter into the extracted species".

In view of the existence of complexes such as $[PtL_2(SnCl_3)Cl]$ and $[PtL_2(SnCl_3)_2]$ [45] (where L = alkyl or aryl phosphines), all of which are reasonably soluble in a variety of organic solvents, Mojski's conclusion may be an oversimplification. It was thus decided to examine in greater detail the effect of $SnCl_2$ on the solvent extractability of platinum(II) by TPP in dichloromethane.

The objectives of this work may now be defined:

(a) To examine the effect of stannous chloride on the extraction of platinum(II) from aqueous hydrochloric acid solutions of K_2PtCl_4 into dichloromethane containing triphenylphosphine.

(b) To devise suitable analytical methods for the determination of platinum(II) and tin(II) in an aqueous acid phase and a dichloromethane phase containing triphenylphosphine.

(c) To propose a mechanism for the extraction of platinum(II) in the presence of tin(II) by examining the effect of the following conditions on the above system:

(i) Time of extraction
(ii) Platinum(II) : Triphenylphosphine ratio
(iii) Platinum(II) : Tin(II) ratio
(iv) Hydrochloric acid concentration.

CHAPTER 2

CHAPTER 2

2. ANALYSIS OF THE AQUEOUS AND ORGANIC PHASES

In order to study in detail the extraction of platinum(II) from hydrochloric acid solutions containing tin(II) chloride it was necessary to devise suitable methods for the analysis of the two metals in the presence of each other in the aqueous acid medium.

It was also desirable to find a method for the accurate determination of platinum(II) and tin(II) in the dichloromethane phase containing triphenylphosphine, so that mass balance could be confirmed.

2.1 Atomic Absorption Determination of Platinum

Atomic absorption spectroscopy has now become a widely used technique for the analysis of over sixty elements [46]. The method is very specific and may be used for trace analysis even in the presence of other elements at much higher concentrations.

The technique relies entirely on the absorption of energy by valence electrons of ground state atoms. Consequently the only common interferences encountered are caused by those chemical and physical processes which inhibit the formation of ground state atoms in the flame. Such interferences are common to all flame spectroscopy techniques and can usually be minimised or eliminated by careful choice of flame type or the use of releasing agents.

Figure 2.1 illustrates simply the principle of atomic absorption spectroscopy.

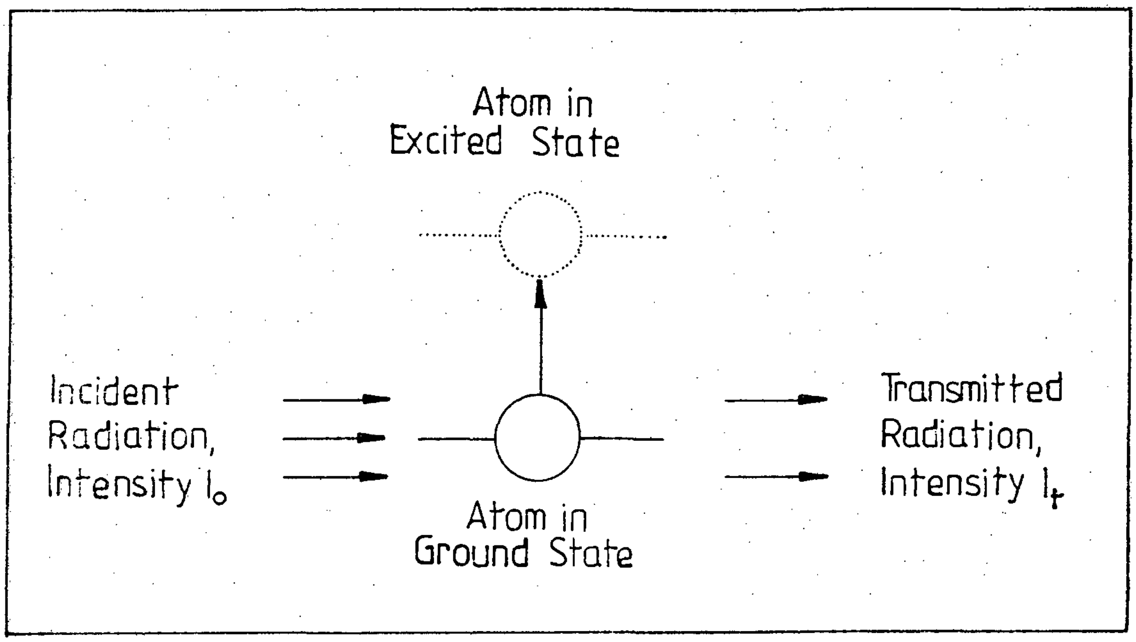


Figure 2.1 A schematic representation of the principle of atomic absorption spectroscopy

The intensity of the transmitted radiation can be represented by Beer's Law:

$$I_t = I_o e^{-(k'cl)}$$

where I_o = intensity of incident radiation

I_t = intensity of transmitted radiation

k' = absorption coefficient at particular wavelength

c = concentration of absorbing atoms

l = length of the absorption path

Therefore, $\log \frac{I_o}{I_t} = k'cl$ = absorbance

That is, the absorbance is proportional to the concentration for a given absorption path length at any given wavelength.

Thus, because of this linear relationship between absorbance and concentration, it is only necessary to compare the absorbance of known standards with that of the sample.

Atomic absorption spectroscopy has been applied to determine platinum in certain organic solvents, for example ethyl acetate [47] and methyl isobutyl ketone [48]. However, a highly chlorinated solvent, such as dichloromethane, is unsuitable due to its poor combustion properties and the fact that it may form phosgene in the flame [49]. It was thus impossible to use atomic absorption spectroscopy for direct analysis of our organic phases.

The method has however been successfully used under certain conditions as an analytical method for determining the platinum group metals in aqueous solutions [50-57]. Air-acetylene mixtures are generally favoured, with very lean, that is strongly oxidising, flames providing maximum sensitivity for platinum. Platinum has a multitude of reasonance lines of which the one at 265,9 nm is the most sensitive.

The determination of the platinum-group metals by this method is subject to a number of serious interferences. For this reason, additives such as $CuSO_4$, $CuCl_2$, $NaHSO_4$, $CuSO_4$ + Na_2SO_4, $CuSO_4$ + $CdSO_4$, KCN, $LaCl_3$, $La(NO_3)_3$, $La_2(SO_4)_3$, U_3O_8, $VOCl_2$, $NdCl_3$, $Nd(NO_3)_3$ and $Nd_2(SO_4)_3$, have been used as releasing agents.

We carried out preliminary investigations using $CuSO_4$ to suppress interferences as this was a cheap and readily available chemical.

Results showing the effect on the absorbance value due to variations in percentage copper sulphate, acid concentration and platinum : tin ratio are shown in Tables 2.1, 2.2 and 2.3. Platinum standards were all prepared from K_2PtCl_4.

$[Pt^{2+}]$/ppm	[HCl]/M	$CuSO_4$/%	Absorbance
500	1,5	0	0,12
	1,5	1	0,70
	1,5	1,6	0,78
	1,5	2	0,78
250	0,75	0	0,38
	0,75	1,5	0,76
	0,75	2	0,80
	0,75	2,5	0,82
	0,75	3	0,83
	0,75	5	0,82

Table 2.1 The effect of percentage $CuSO_4$ on the absorbance of platinum solutions at particular acid concentrations.

From results obtained in Tables 2.1 and 2.2 it is evident that the use of 2% copper sulphate would successfully suppress interferences in determining platinum by atomic absorption.

However, Table 2.3 shows that addition of stannous chloride seriously affected the readings obtained. We attributed this to the reduction

$[Pt^{2+}]$/ppm	[HCl]/M	Absorbance
500	1,5	0,87
	3	0,80
	5	0,80
300	1,5	0,69
	3	0,62
	5	0,63

Table 2.2 The effect of hydrochloric acid on the absorbance of platinum solutions containing 2% $CuSO_4$.

$[Pt^{2+}]$/ppm	Pt:Sn ratio	Absorbance
500	1:0	0,98
	1:4	0,83
	1:5	0,83
	1:10	0,65

Table 2.3 The effect of $SnCl_2$ on the absorbance of platinum solutions in 1,5 M HCl with 2 % $CuSO_4$.

of copper(II) by tin(II):

$$Sn^{2+} + 2Cu^{2+} \rightarrow Sn^{4+} + 2Cu^{+}$$

This conclusion was supported by the fact that, after preparation, solutions containing platinum:tin ratios of 1:4 and 1:5 faded rapidly from deep red to blue/green. It was this rapid reduction of copper(II) by the tin(II) which rendered the copper sulphate useless as an interference suppressant for platinum in this work.

Vasilyeva *et al* [57] suggested the use of lanthanum and neodymium nitrates as suitable compounds for suppressing interferences in platinum determinations by atomic absorption. We therefore carried out investigations on the use of lanthanum nitrate as an inteference suppressant. Results showing the effect on the absorbance value due to variations in lanthanum nitrate concentration, the acid strength and the platinum:tin ratio are shown in Tables 2.4 and 2.5.

$[Pt^{2+}]$/ppm	$La(NO_3)_3$/%	Absorbance
227	0,2	0,83
	0,4	0,83
124	0,2	0,52
	0,4	0,52
83	0,2	0,37
	0,4	0,36

Table 2.4 The effect of percentage $La(NO_3)_3$ on the absorbance of platinum in 1,5 M HCl containing $SnCl_2$ at a Pt:Sn ratio of 1:2.

$[Pt^{2+}]$/ppm	Pt:Sn ratio	[HCl]/M	Absorbance
250	1:0	3	0,71
	1:2	3	0,66
	1:5	3	0,67
	1:10	3	0,65
250	1:0	1	0,70
	1:2	1	0,69
	1:5	1	0,69
	1:10	1	0,71
63	1:0	3	0,24
	1:2	3	0,24
	1:5	3	0,24
	1:10	3	0,24
63	1:0	1	0,24
	1:5	1	0,25

Table 2.5 The effect of hydrochloric acid and stannous chloride on the absorbance of platinum solutions with 0,2% $La(NO_3)_3$.

Results from Tables 2.4 and 2.5 show that 0,2% lanthanum nitrate is suitable to suppress interferences in platinum solutions of 1-3 M hydrochloric acid with tin:platinum ratios of up to 10.

Experiments also showed that more accurate results were obtained if standards were made up containing tin(II) in approximately the same concentration as the samples. Table 2.6 shows a few results to illustrate the better precision obtained in this way.

	Pt:Sn ratio	$[Pt^{2+}]$ taken/ppm	$[Pt^{2+}]$ found/ppm	Relative % error
Platinum standards without tin	1:5	74	70	5,7
	1:2	92	89	3,3
Platinum standards with tin (Pt:Sn=1:2)	1:2	165	167	1,2
	1:2	145	145	0

Table 2.6 Comparison of relative percentage errors obtained for samples using platinum standards with and without tin(II) chloride at 1,5 M HCl.

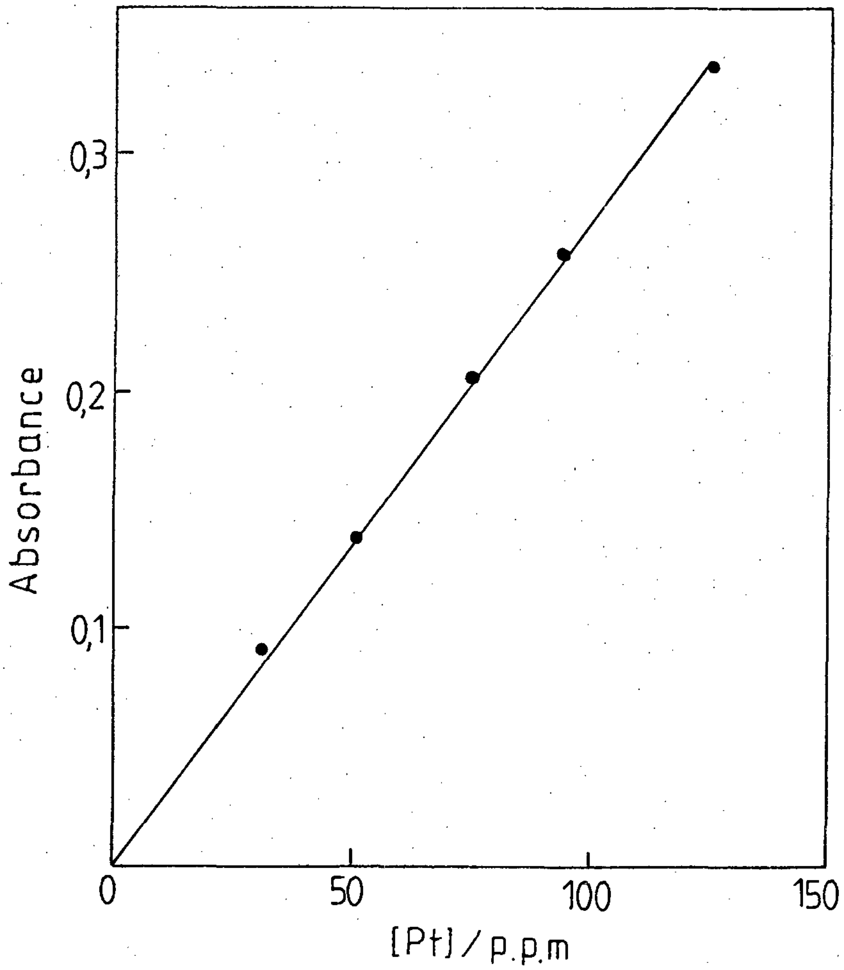


Figure 2.2 A calibration curve for platinum in 1,5 M HCl with 0,2% $La(NO_3)_3$ and stannous chloride (Sn/Pt ratio = 2).

We thus chose to prepare our platinum standards from K_2PtCl_4 with 0,2% $La(NO_3)_3$ in the presence of tin(II) chloride and hydrochloric acid of appropriate concentrations so as to match the matrix as closely to that of the samples as possible. We found that under these conditions Beer's Law was obeyed for 0-150 p.p.m. of platinum. A typical calibration curve obtained in this way is shown in Figure 2.2.

2.2 Atomic Absorption Determination of Tin

Tin may be determined relatively easily in hydrochloric acid solutions by the atomic absorption method [58-63]. However, as described in Section 2.1, it was not possible to analyse the dichloromethane extracts directly by this method.

A variety of different flames have been used, including air-acetylene, air-hydrogen, argon-hydrogen, nitrous oxide-acetylene and nitrogen-hydrogen-entrained air. A strongly reducing air-acetylene flame was used in our work since this is a convenient method and has been found to be less subject to interferences despite its lower sensitivity compared with other flames [62]. Readings were taken at a wavelength of 286,3 nm.

Figure 2.3 shows a typical calibration curve using standards in 10% hydrochloric acid prepared from tin metal. Results in Table 2.7 show that platinum does not interfere in the determination of tin in 10% hydrochloric acid solutions.

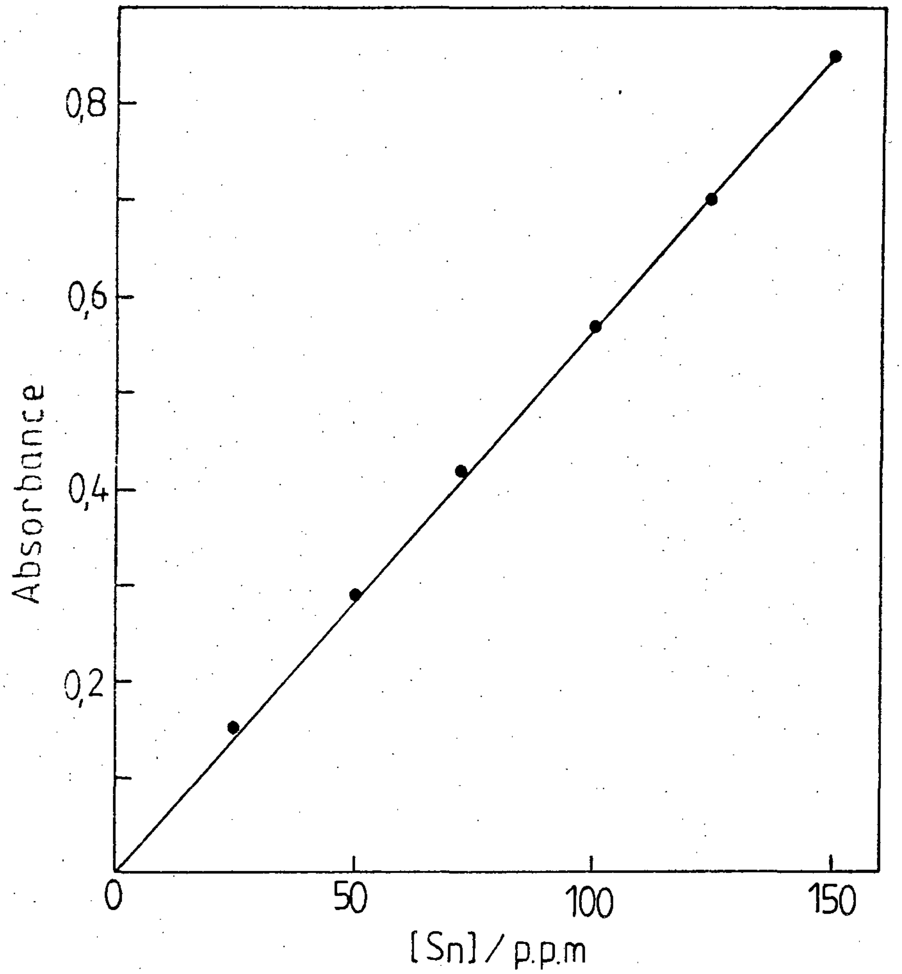


Figure 2.3 · Calibration curve for tin in 10% HCl solution

Pt:Sn ratio	[Sn] taken/ ppm	[Sn] found/ ppm	Relative percentage error
1:1	83	83,5	0,6
1:2	57,4	57,1	0,5
1:2	92	91,8	0,3
1:2	51,2	51,3	0,2
1:5	42	42	0

Table 2.7 The effect of platinum on the determination of tin in 10% HCl.

The determination of tin in the aqueous phase by atomic absorption was thus found to be a suitable method since the concentration of tin could be accurately determined in the presence of platinum.

2.3 Oxidation with Potassium Iodate

The titrimetric determination of tin(II) in hydrochloric acid by oxidation with potassium iodate is a well-documented method [64-66]. The procedure involves the use of an immiscible organic solvent, such as chloroform, with the end point being marked by the disappearance of the last trace of violet colour, due to iodine, from the organic layer. The oxidation is thought to proceed through the following steps:

$$30SnCl_2 + 10KIO_3 + 60HCl \rightarrow 30SnCl_4 + 10KI + 30H_2O$$

$$2KIO_3 + 10KI + 12HCl \rightarrow 12KCl + 6H_2O + 6I_2$$

$$3KIO_3 + 6I_2 + 18HCl \rightarrow 3KCl + 9H_2O + 15ICl$$

The overall reaction may thus be represented as:

$$2SnCl_2 + KIO_3 + 6HCl \rightarrow 2SnCl_4 + KCl + ICl + 3H_2O$$

Although atomic absorption determinations of tin in the aqueous phase had proved successful, this method reflects the total amount of tin present, that is, tin(II) and tin(IV). Since we believe that it is mainly tin(II) which is involved in the formation of the red platinum-tin complex, it was necessary to know the exact amount of tin(II) present in an aqueous layer. For this reason we decided to investigate whether the potassium iodate titration could be used to determine tin(II) in the presence of platinum(II).

We found in fact that titration of freshly mixed stannous chloride and K_2PtCl_4 solutions in concentrated hydrochloric acid with potassium iodate led to the complete oxidation of both tin(II) and platinum(II). The intense red colour of solutions containing platinum and tin faded during addition of the potassium iodate, allowing for easy detection of the violet colour in the organic layer.

We also found that oxidation with iodate may be used to determine platinum(II) quantitatively in solutions of this metal. The stoichiometry of the process may be represented as:

$$2K_2PtCl_4 + KIO_3 + 6HCl \rightarrow 2K_2PtCl_6 + KCl + ICl + 3H_2O$$

Although initial development of colour in the chloroform layer was slow for solutions containing platinum, the final end point was in fact very sharp.

Some typical titration results are shown in Table 2.8. Since tin(II) is easily oxidised by the oxygen in air, all titrations were performed under nitrogen. This suggested the possibility of oxidising only the tin(II) by bubbling air or oxygen through the mixed K_2PtCl_4/stannous chloride solutions. A subsequent experiment showed that only the tin(II) species could be destroyed by selectively oxidising it to tin(IV) using oxygen for 35 minutes, followed by titration with KIO_3 to determine the amount of platinum(II) left in solution.

Sn(II) taken/ mmol	Pt(II) taken/ mmol	Total oxidisable species/mmol	Volumes KIO_3 used/ ml	Mean titre/ ml KIO_3	Total oxidisable species found/mmol
0,2200	-	0,2200	9,51 9,49 9,50	9,50	0,2071
0,7550	-	0,7550	13,23 13,28 13,26	13,26	0,7346
-	0,0650	0,0650	2,91 2,95 2,97	2,94	0,0645
-	0,0950	0,0950	4,41 4,40 4,36	4,39	0,0957
0,4142	0,0950	0,5092	23,40 23,33 23,40	23,38	0,5095
0,1192	0,0255	0,1447	14,63 14,58 14,61	14,61	0,1429

Table 2.8 Results of platinum(II) and tin(II) determinations by potassium iodate titration.

Time of contact with oxygen/mins.	Sn(II) taken/ mmol	Pt(II) taken mmol	Oxidisable species found / mmol
35	-	0,1320	0,1312
35	-	0,1346	0,1358
15	0,6930	0,1346	0,1423
20	0,6930	0,1346	0,1380
35	0,6930	0,1346	0,1323
35	0,6930	0,2640	0,2596
35	0,6930	0,1320	0,1329

Table 2.9 Results obtained after oxidation of K_2PtCl_4 and stannous chloride solutions with oxygen in 3M HCl for various time intervals and subsequent titration with KIO_3.

Table 2.9 shows that after this time interval, the tin(II) is completely oxidised and the remaining platinum(II) may be quantitatively determined to less than 2% error.

It appeared therefore that this would be an extremely useful and convenient method for the determination of platinum(II) and tin(II) in the aqueous phase. We thus decided to apply this method extensively for the determination of tin(II) in our extraction experiments and time was spent in order to perfect the procedure.

Attempts were made to oxidise the tin(II) by other methods. However, copper(II) and hydrogen peroxide used for this purpose were found to interfere in the titrimetric procedure and we therefore decided to continue using oxygen.

Although detailed studies were not carried out to determine the effect of acid concentration on the titration, suitable conditions were found by trial and error. Vogel [64] reports that the optimum acidity for a reasonably rapid reaction near the end point varies from one reductant to another within the range of 2,5-9 M hydrochloric acid. The conditions for the iodate oxidation of tin(II) described by Vogel involve acid concentrations of about 5M. We found that the most suitable range of acid concentration for the mixture of tin(II) and platinum(II) was 5-6,5 M, whereas for platinum(II) only, acid concentrations of about 4,5 M were used.

Unfortunately, however, on attempting to titrate portions of the aqueous metal solutions as described above after preliminary extraction experiments with triphenylphosphine, no violet colour developed in the chloroform layer and it was thus impossible to obtain an end point. Titration of a portion of the platinum-tin solutions shaken with dichloromethane in the absence of phosphine resulted in an extremely slow development (15-20 minutes) of the violet colour in the chloroform layer, but results obtained were found to be unreproducible.

It thus appeared that, after shaking, the platinum-tin complexes had reached equilibrium resulting in very slow oxidation by potassium iodate. The freshly-mixed solutions had not been equilibrated and although some $SnCl_3^-$ was bound to $PtCl_4^{2-}$ in this case, the red complexes had not in fact completely formed. (See below in Section 3.1).

Triphenylphosphine can be oxidised by nitric acid to form phosphine oxide, $O = P(Ph)_3$ [67]. It was therefore reasonable to expect that the compound could also be oxidised by iodate in a similar way. To investigate this proposal, samples of triphenylphosphine were weighed accurately, dissolved in CH_2Cl_2 in the titration flask, HCl was added and the mixture was titrated with potassium iodate. Colour changes during titration showed that, as predicted, some reaction did occur with the phosphine. The presence of any triphenylphosphine-containing compounds in the aqueous phase would therefore have caused serious errors in the determinations.

Although this method was reproducible and reliable in the case of freshly-mixed solutions there were complications with solutions which had been shaken in the presence of the organic phase containing triphenylphosphine. We could unfortunately not continue to use this procedure for our determinations. However, it may be that with further investigation the method could well prove useful for the analysis of platinum(II) and tin(II) solutions which do not contain any interfering substances.

2.4 Polarography

Polarography is an electrochemical analysis method introduced by Heyrovský some 50 years ago, for the qualitative and quantitative determination of substances in solution [68,69]. The method is useful for the analysis of small amounts of substances, usually about $10^{-5}-10^{-2}$M sample solutions. The method can be used to determine inorganic ions that are reducable to lower oxidation states, as well as to determine numerous organic compounds.

In DC polarography, a DC voltage increasing or decreasing as a linear function of time is applied across the measuring cell whereas in AC polarography a small, low-frequency AC voltage is superimposed upon the DC voltage ramp. Two different polarograms are obtained in each case. Two quantities appear on a polarogram which are related to the kind and quantity of the dissolved substance (depolariser), namely the half-step potential $E_{\frac{1}{2}}$ and the wave height, or limiting diffusion current, i_d. The latter is proportional to the concentration of the depolariser and the quantity of the sample substance may be determined from the i_d by three different methods, namely: standard addition, recording a calibration curve and by calculation using Ilkovic's equation.

Procedures for the polarographic determination of tin as the stannous and stannic ion have been described [70,71]. We decided to investigate whether this method could be used for the measurement of tin(II) in our aqueous phases containing K_2PtCl_4 and $SnCl_2$.

Both stannous and stannic tin can be reduced at the dropping mercury electrode. Love and Sun [71] reported that reduction of stannous tin to the metal produces waves suitable for analytical purposes in supporting electrolytes of tartrate and alkaline citrate as well as 1N solutions of hydrochloric acid, nitric acid, sulphuric acid and sodium hydroxide. The reduction of stannic tin produced waves suitable for analytical purposes only in hydrochloric acid solutions where the concentration of chloride ion is greater than about 4N. Stannic tin produces a double wave, corresponding to stepwise reduction first to the stannous state and then to the metal, with half-wave potentials of -0,25 and -0,52 volt v.s. the saturated calomel electrode. Figure 2.5 shows a typical DC polarogram of stannic tin in ammonium chloride and

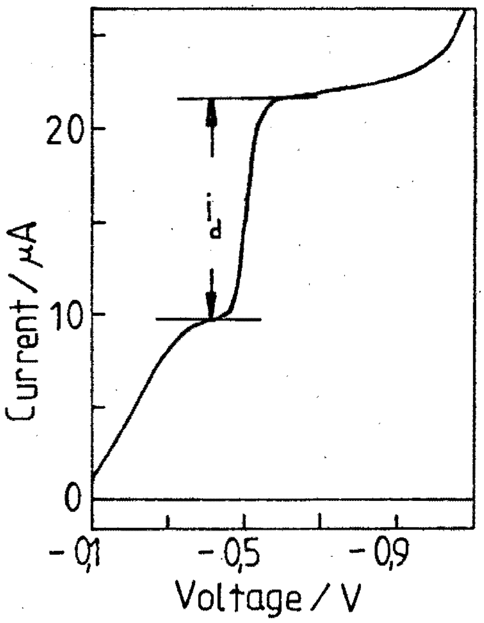


Figure 2.5 Typical polarogram of stannic tin (2,08 mmol) in 4 M ammonium chloride, 1M hydrochloric acid and 0,005% gelatine. (Reproduced from reference 70).

hydrochloric acid. Since it has been shown that better reproducibility can be obtained with AC than with DC polarography [72], we investigated the possibility of using the former method to determine tin(II) in our aqueous phase. Figure 2.6 shows that in the absence of platinum, a single well-defined wave was obtained at -0,315 V probably due to reduction of stannous ion to the zero oxidation state.

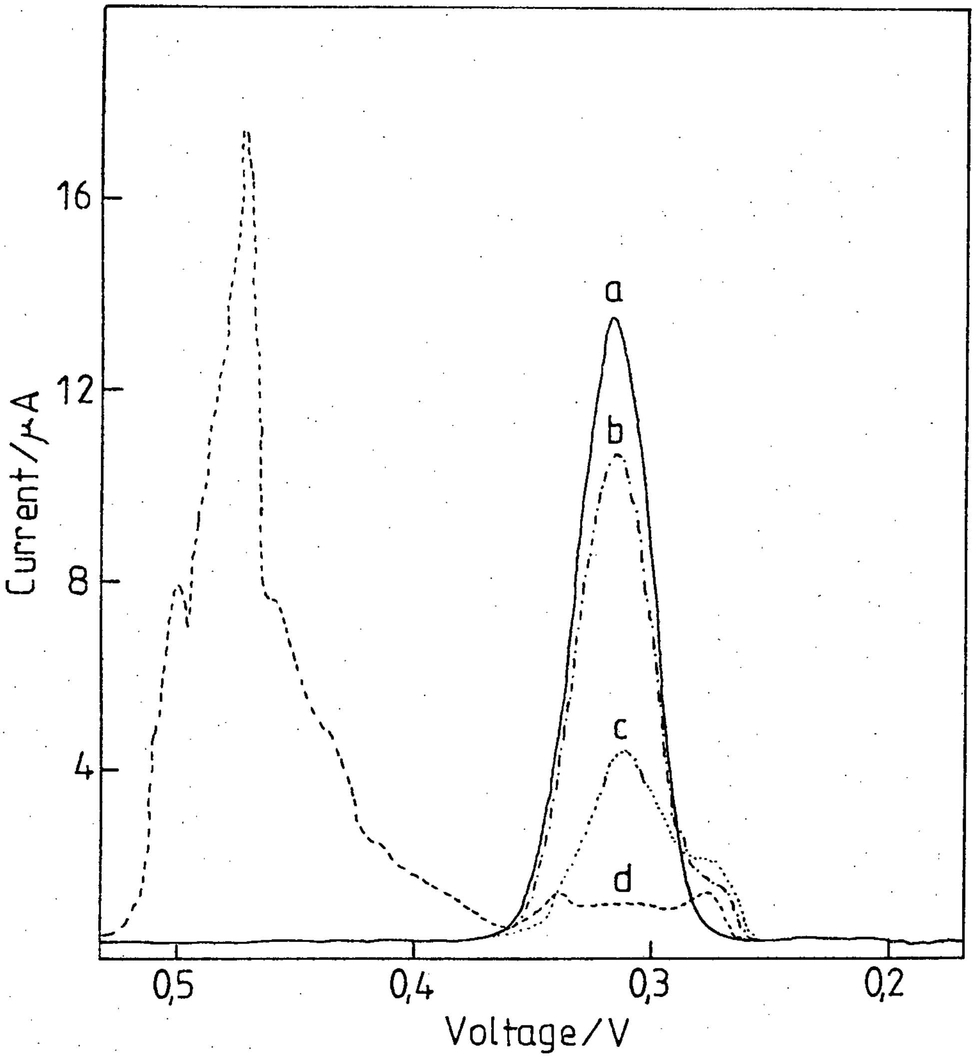


Figure 2.6 Polarograms of a solution of stannous chloride (0,228 mmol) in 1 M hydrochloric acid and 0,005% gelatine to show the effect of successive additions of K_2PtCl_4 (0,014 M in 1 M HCl). (a) Polarogram of tin solution, (b) - (d) Polarograms after additions of 1,2,4 ml of Pt solution respectively.

Unfortunately, the wave due to tin was seriously affected on addition of small amounts of platinum to this solution and the wave height could not be accurately measured. The dark deposit which appeared on addition of platinum was presumably a cause of the complications.

Experiments were also carried out using other supporting electrolytes, such as one of 4 M ammonium chloride, 1 M hydrochloric acid and 0,005% gelatine but similar problems were experienced.

Kivalo and Laitinen [73] have shown that the polarographic reduction of K_2PtCl_4 is in fact very complex. Thus, due to the difficulties experienced, a polarographic method for the determination of tin(II) could unfortunately not be used in our case.

2.5 Ashing of the Organic Phase

Experiments were carried out to establish whether platinum could be determined in the organic phase after removal of the dichloromethane by evaporation and ashing of the remaining solid to remove the carbon and tin [74].

After a preliminary extraction experiment, the organic phase was transferred to a crucible, the dichloromethane was removed and the sample was ashed. The residue was heated vigorously with *aqua regia*, the solution was made up volumetrically and the amount of platinum determined by atomic absorption.

Table 2.10 shows the result of two such random experiments.

Time of extraction/ hours	Total Pt taken / ppm	Pt found / ppm Aqueous phase	Pt found / ppm Organic phase	Total Pt found / ppm	% Error
$\frac{1}{2}$	124	91	37	128	3,1
18	124	27	102	129	3,6

Table 2.10 The determination of platinum by atomic absorption in the aqueous and organic phases after extraction of a 1 M HCl phase of Sn/Pt ratio 2 with dichloromethane containing PPh_3/Pt ratio 3.

Table 2.10 shows that mass balance for platinum in the two phases does in fact hold. Results thus show that, allowing for a 4% error, ashing of the organic phase is a suitable method for the determination of platinum in the organic phase.

2.6 The Distillation of Tin

Tin has been separated by distillation with hydrochloric-hydrobromic acid and subsequently colourimetrically determined with dithiol [75] or titration with potassium iodate after reduction with nickel [76]. We decided to attempt using the procedure for the determination of tin in our organic phases. A method involving ashing of the organic residue was unsuitable due to the volatility of the tin(IV) chloride.

After extraction the dichloromethane phase was transferred to a distillation flask and gently warmed to evaporate the solvent. The distillation with hydrochloric and hydrobromic acid was then carefully carried out. It was hoped to use atomic absorption for the analysis of the distillate.

However, repeated attempts under various conditions to perform a quantitative distillation proved unsuccessful. Qualitative tests with hydrogen sulphide [77] showed that in all cases tin was still present in the initial distillation flask.

It thus appeared that formation of platinum-tin complexes and the presence of triphenylphosphine unfortunately seriously affected this method for the analytical determination of tin.

.7 Conclusion

The atomic absorption method was chosen for the analysis of tin and platinum in the aqueous phases. Results obtained in this way proved to be the most reliable and reproducible and allowed for an easy and rapid determination of the metals.

The titrimetric method of oxidation with potassium iodate was used only to determine the percentage tin(II) present in the unmixed stannous chloride solutions.

By evaporation and ashing of the organic phase and subsequent use of atomic absorption, we were able to determine reliably the amount of platinum extracted into this layer. Mass balance was confirmed using this procedure. However, since the method was quite lengthy and tedious, the mass balance was not checked repeatedly for all extractions in this way. Unfortunately we were unable to find a suitable method for the direct determination of tin in the organic phase. However, throughout the extraction experiments samples were compared with a blank. This provided an efficient way of comparing our aqueous layers after extraction with TPP, with an identical solution shaken with pure dichloromethane.

CHAPTER 3

CHAPTER 3

. SOLVENT EXTRACTION STUDIES

Having established suitable analytical methods for the determination of tin and platinum, we proceeded to make a detailed study of the extraction of platinum from acid solutions containing stannous chloride using triphenylphosphine in dichloromethane. All work was carried out under nitrogen and strict precautions were taken to exclude air at all times. Details of the actual experimental procedures are given in Chapter 5.

3.1 Preliminary Investigations

3.1.1 *Equilibration of the Aqueous Phase*

When solutions of $PtCl_4^{2-}$ and $SnCl_2$ are mixed in HCl the colour of the mixture gradually becomes more intense, so that sufficient time must be allowed for equilibrium to be reached.

Freshly prepared aqueous solutions containing a tin:platinum ratio of 2 at various acid concentrations were shaken with dichloromethane and the UV-visible absorption spectra of the aqueous phase were determined as a function of time.

For solutions of 1 M hydrochloric acid concentration, equilibrium was reached in 10 minutes. The visible absorption spectrum (Figure 3.1) shows three distinct maxima at 373 ($\varepsilon_{max} = 8{,}52 \times 10^6$ cm^2 mol^{-1}),

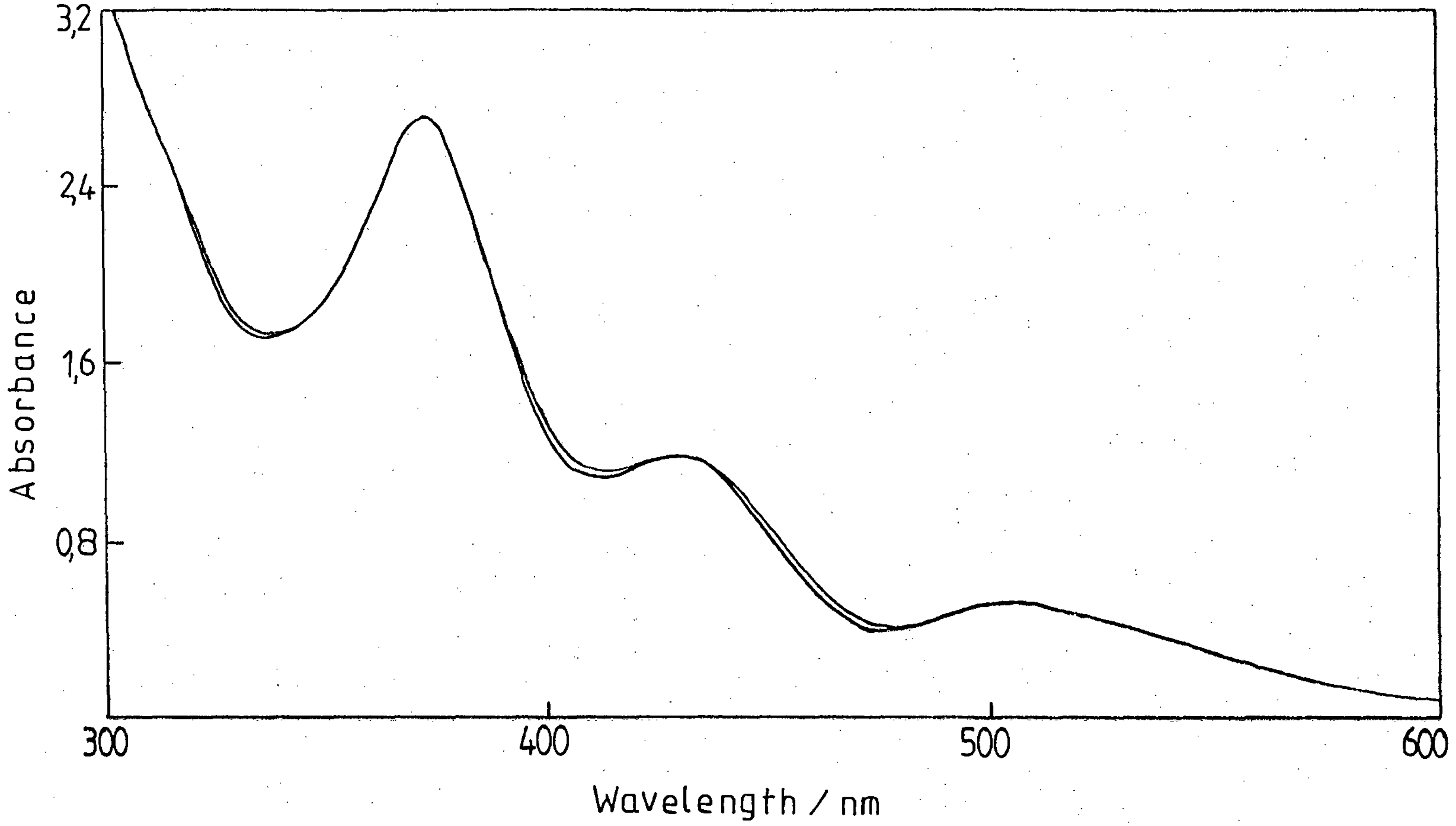


Figure 3.1. Visible absorption spectrum for solutions of Sn(II)/Pt(II) ratio of 2 at 1 M HCl. Repeated scans every 10 minutes for 10-40 minutes.

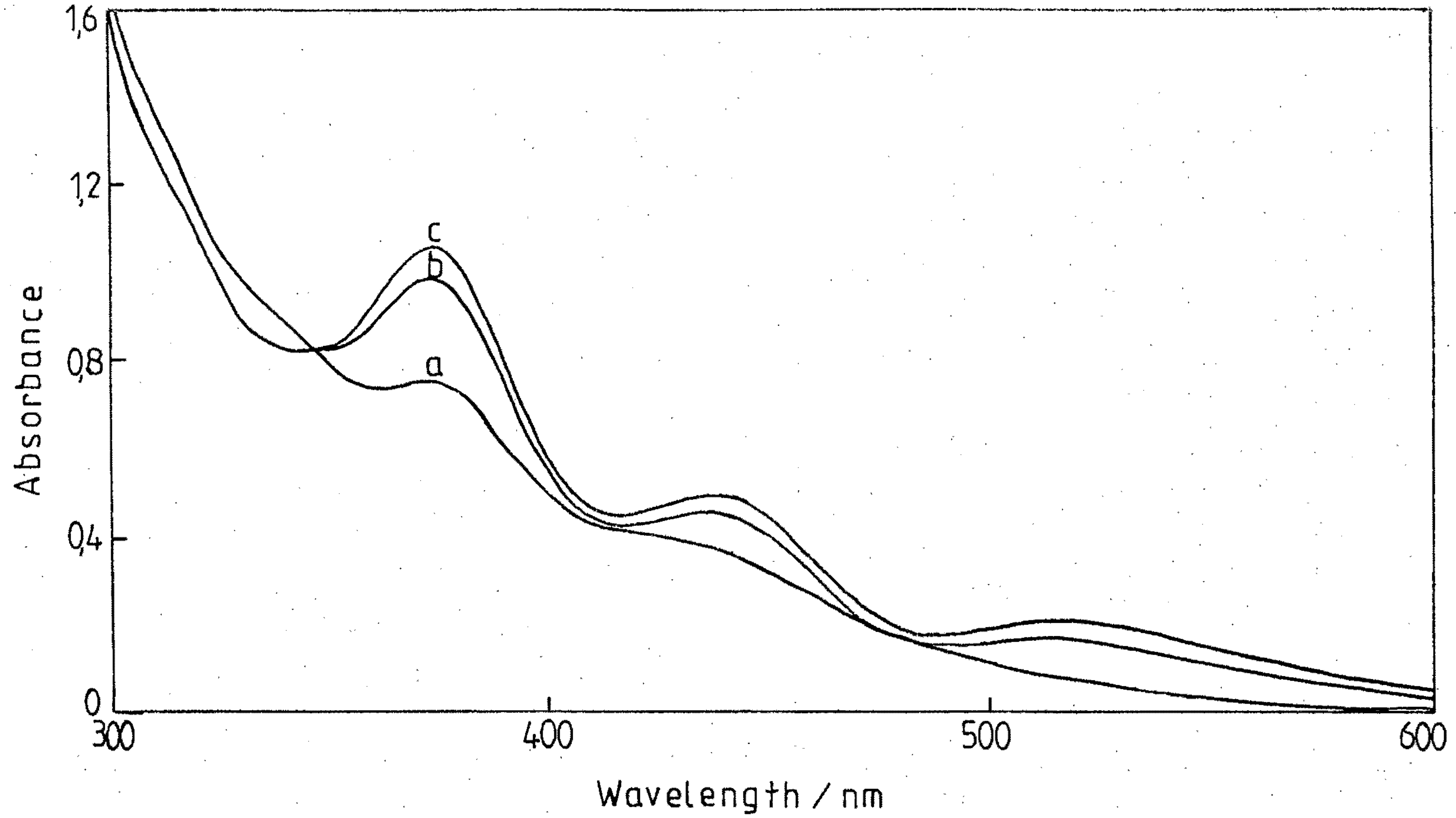


Figure 3.2 Visible absorption spectrum for aqueous solutions of Sn(II)/Pt(II) ratio 2 at 1,5 M HCl. Scans after (a) 2 minutes (b) 10 minutes (c) 20-50 minutes.

431 (ε_{max} = 3,71 x 10^6 cm^2 mol^{-1}) and 506 nm (ε_{max} = 1,63 x 10^6 cm^2 mol^{-1}). Repeated scans every 10 minutes from 10-40 minutes showed that the spectrum did not change significantly.

In the case of solutions at 1,5 M HCl, equilibrium was reached after 20 minutes of shaking as shown in Figure 3.2. The three absorption maxima are at 374, 438 and 517 nm with molar extinction coefficients for the equilibrated state of 3,79 x 10^6, 1,75 x 10^6 and 7,5 x 10^5 cm^2 mol^{-1} respectively.

Day old solutions under the same conditions and at 1,5 M HCl were also found to reach equilibrium after 20 minutes but the absorbances were found to be slightly lower than the freshly prepared solutions. (Molar extinction coefficients at the wavelengths 374, 438 and 517 nm are 2,96 x 10^6, 1,36 x 10^6 and 5,7 x 10^5 cm^2 mol^{-1} respectively). This effect was most probably due to oxidation by oxygen of a small percentage of the tin(II) in the stannous chloride solution.

The absorption spectra of mixed platinum and tin solutions at acid concentrations of 2,3 M and 6 M were found to be more complicated probably due to the faster oxidation of tin(II) at the higher acidities. Figure 3.3 shows the absorption spectra of a solution of 2,3 M HCl at various times after mixing. The spectra appear to be complicated in that the peaks at 253 and 308 nm grow with time, whereas the peak at 384 nm decreases accordingly; and no steady state was reached. The colour intensity of solutions at 6 M HCl decreased rapidly with time and peaks were found to be broad at this high acidity (Figure 3.4).

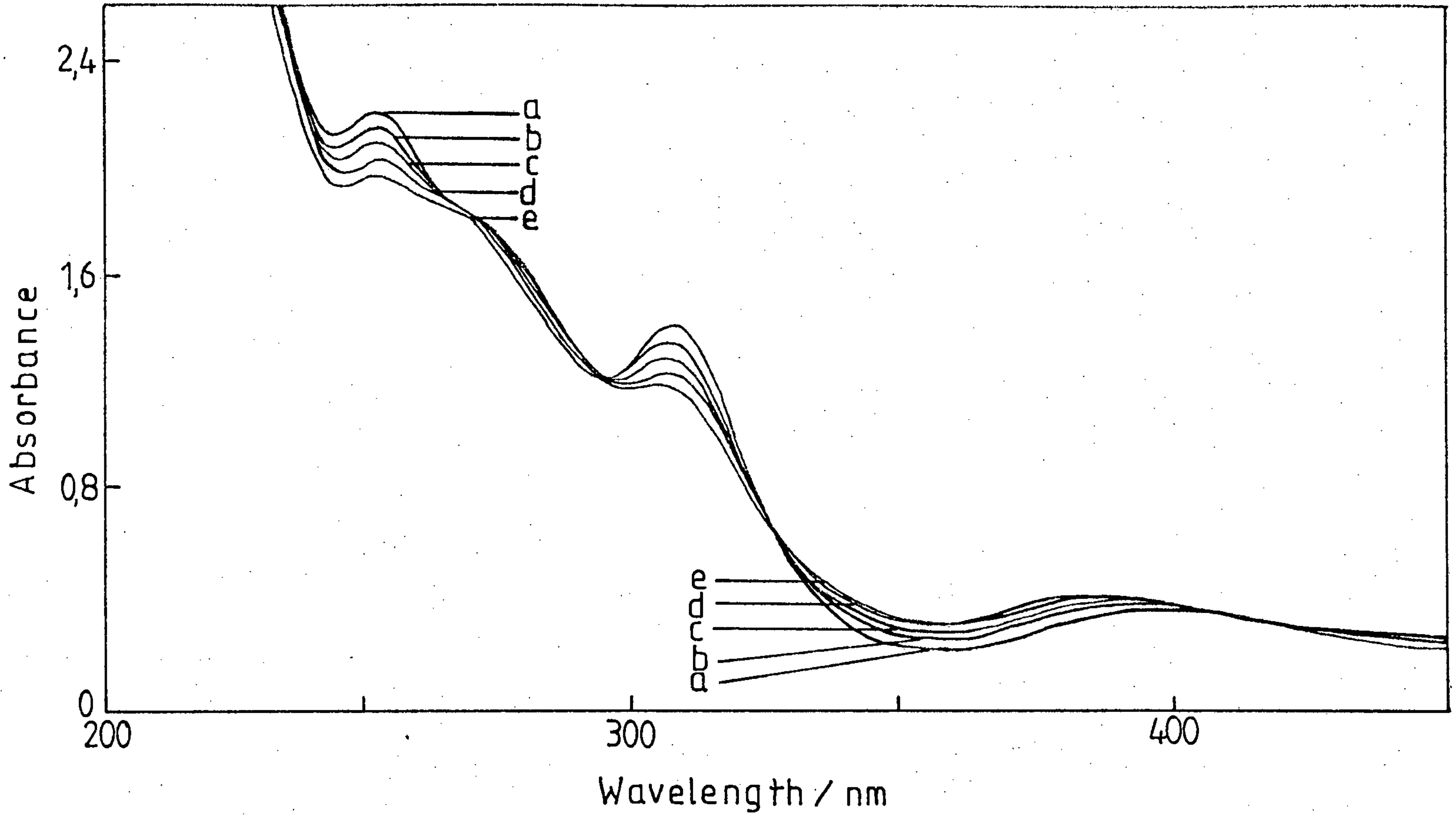


Figure 3.3 Visible absorption spectrum for aqueous solutions of Sn(II)/Pt(II) ratio of 2 at 2,3 M HCl. Spectra (a)-(e) represent scans from 20-100 minutes respectively, at time intervals of 20 minutes each.

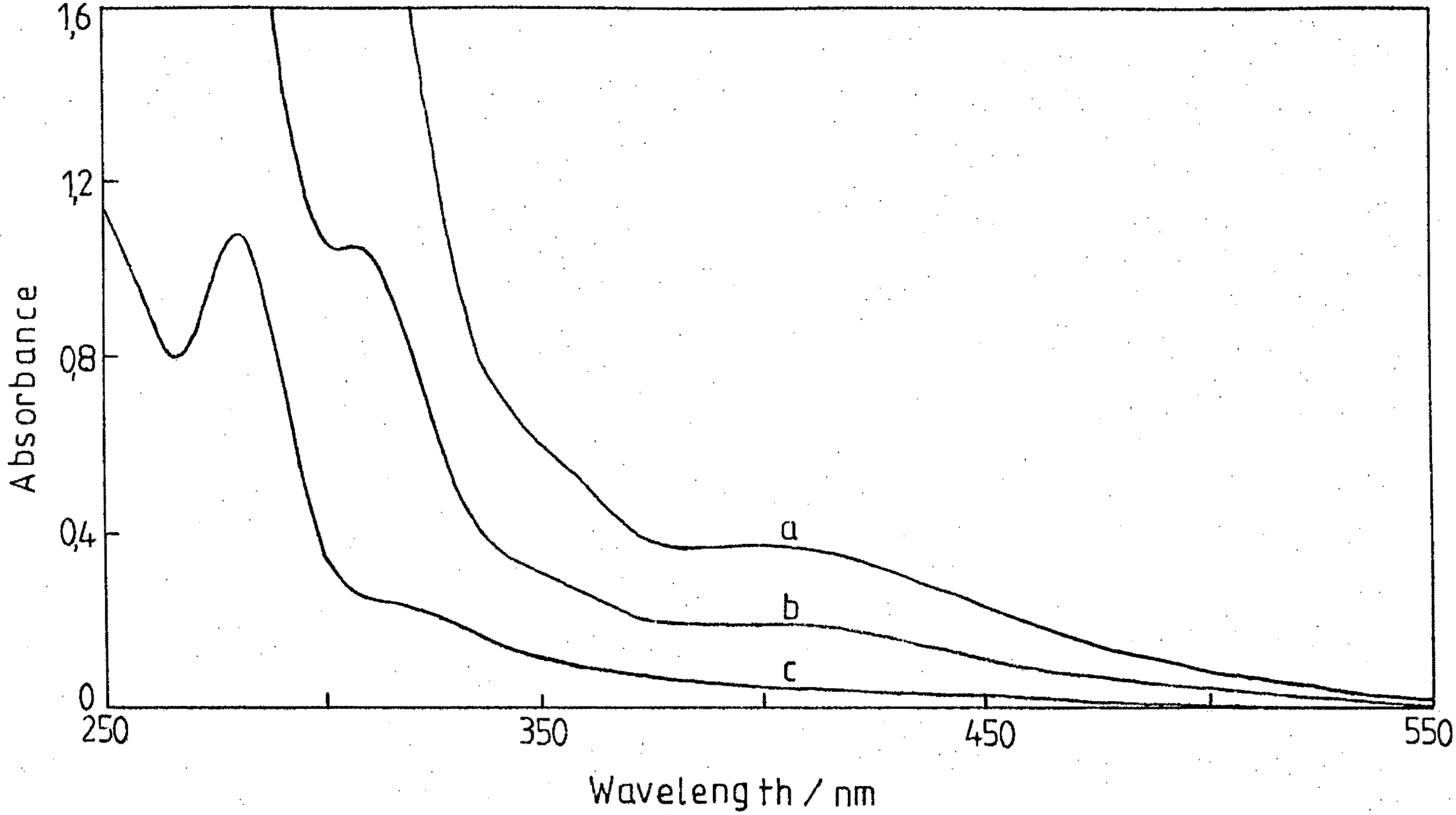


Figure 3.4 Visible absorption spectrum for aqueous solutions of Sn(II)/Pt(II) ratio 2 at 6 M HCl. Spectra represent scans after time intervals of (a) 10 minutes (b) 20 minutes (c) 40 minutes.

Tompkins and Lachman [78] have shown that the rate of oxidation of $SnCl_2$ is proportional to $[HSnCl_3]^{\frac{1}{2}}$ and is therefore dependent on the acid concentration. The fairly rapid fading observed in solutions at 2,3 and 6 M HCl is explainable by this oxidation process. Since it was extremely difficult to keep the extraction vessels totally free of oxygen, these acid concentrations were obviously unsuitable for our purposes.

Solutions of platinum(II) with $SnCl_3^-$ are known to be unstable at low acid concentrations as a result of hydrolysis to form complexes of the type M_{n-2} $[Pt\{Sn(OH)_3\}_n]$, where M = H^+, Na^+, K^+ etc and n = 4 or 5 [79]. The original red complex is converted to a brown residue under such conditions. Stock solutions of stannous chloride must also be prepared in sufficiently acidic solutions to prevent precipitation of the basic chlorides of tin [80].

We therefore chose to use platinum and tin solutions of 1 M and 1,5 M HCl throughout our work, allowing for an initial equilibration period of 10 and 20 minutes respectively, before addition of the organic phase.

3.1.2 *Ultraviolet-visible Spectrophotometry*

As described in Section 1.1, stannous chloride has been used as an important colourimetric reagent for the determination of platinum. It was therefore reasonable to expect that this property might be useful to determine the platinum content in the aqueous phase.

Sets of experiments were carried out by initially equilibrating the aqueous acid phases of platinum and tin as described in Section 3.1.1. The aqueous layers were then shaken with equal volumes of dichloromethane containing TPP for various time periods. The phases were separated and the absorption spectrum of the particular layer was determined immediately. For comparison purposes, a blank was included in all experiments. Absorption spectra were recorded for samples from a number of sets of experiments. A typical example to show the general decrease in absorbance with time of shaking is illustrated in Figure 3.5. Table 3.1 compares the percentage extraction determined from atomic absorption with that obtained from the uv-visible spectra for the set of experiments illustrated in Figure 3.5. The percentage extraction in the latter case was calculated from the decrease in the absorbance at the 373 nm maximum using a blank as the initial measurement.

Time of extraction/ hours	Percentage extraction of Pt	
	From atomic absorption	From uv-visible spectrum
½	14,9	5,8
1	19,4	11,3
1½	30,7	26,8
2½	51,9	43,2
3	65,3	49,3
18	98,1	83,6

Table 3.1 A comparison of the percentage extraction values obtained by atomic absorption and uv-visible spectrophotometry.

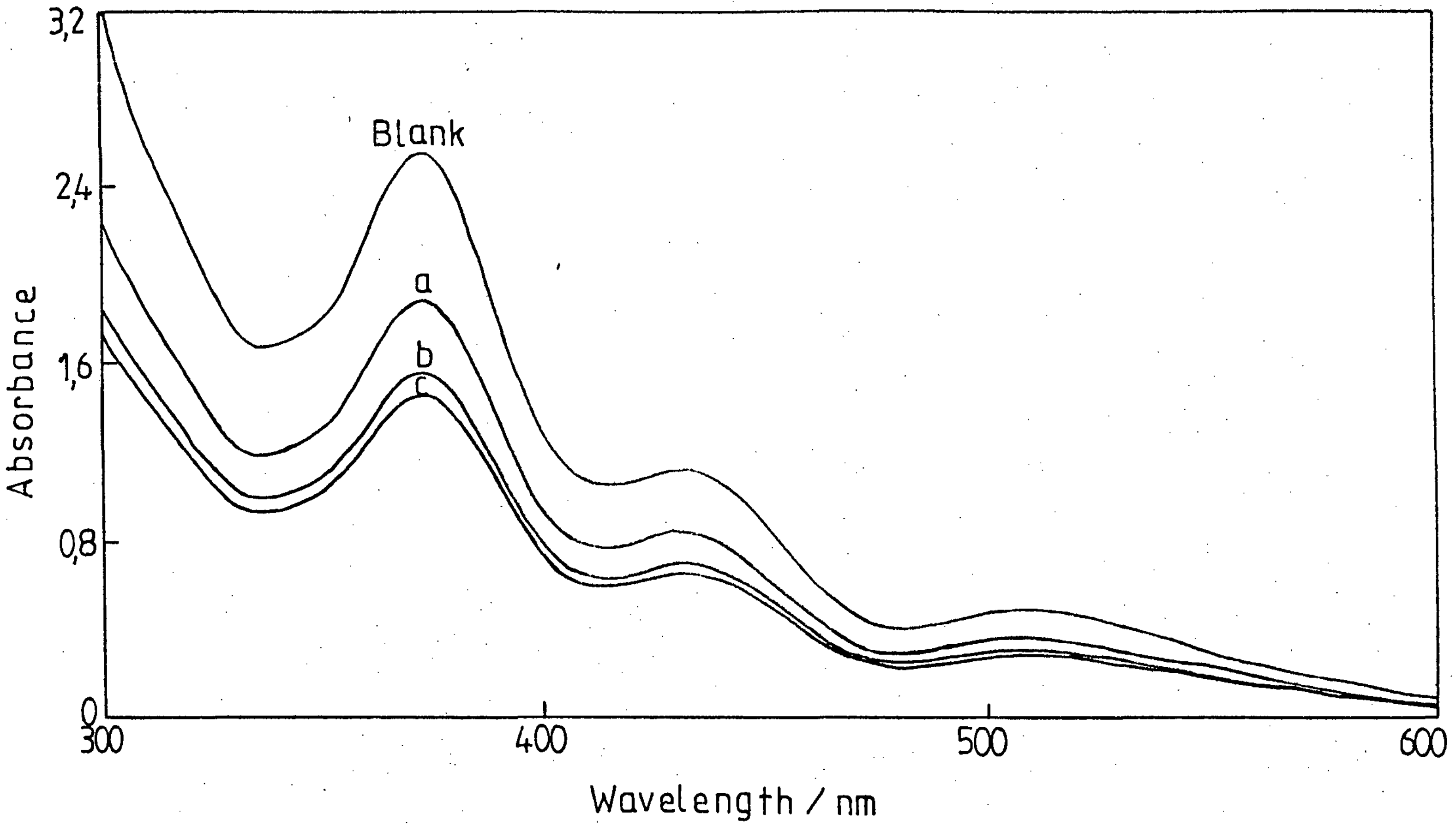


Figure 3.5 The absorption spectra of the aqueous phases after extraction of a solution of Sn(II)/Pt(II) ratio 2 in 1 M HCl with TPP in CH_2Cl_2 (TPP/Pt ratio = 4). Time periods of extraction: (a) 1½ hours (b) 2½ hours (c) 3 hours.

Results showed that although a general decrease in colour intensity was observed in a particular set of extractions with time, the change in peak height did not appear to be directly related to the platinum concentration, as found by atomic absorption. A possible reason for this is that the colour of the solutions is extremely sensitive to air and although precautions were taken to exclude air at all times, traces of oxygen may well have been present.

The organic phase was found to vary in colour from very pale yellow to orange. We therefore also investigated the possibility of using the absorbance of the organic phase as a means of analysing the organic extract.

Figure 3.6 illustrates that the colour intensity of the CH_2Cl_2 layer fades rapidly with time even though sealed sample cells were used and strict precautions were taken to exclude air. The peaks were also poorly defined in most cases. It is thus evident that the absorption spectra of the aqueous and organic extracts could not be used for quantitative purposes since it was extremely difficult to exclude small amounts of oxygen. Nevertheless the colour of the two phases was found to be useful, in that it was possible to monitor visually the course of a solvent extraction.

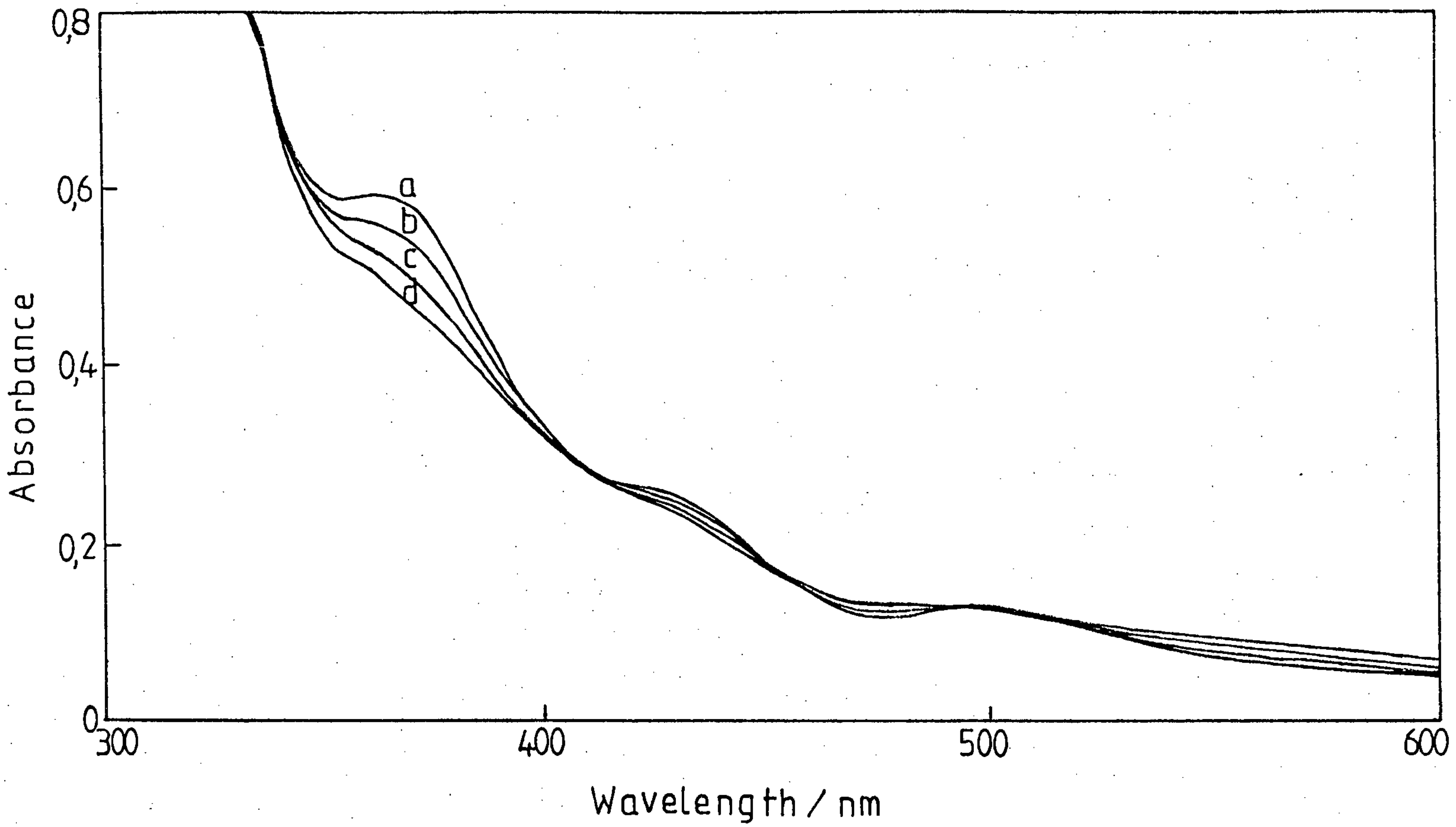


Figure 3.6 Absorption spectra of dichloromethane layers after extraction for 20 minutes at conditions: (i) Sn(II)/Pt(II) ratio 2 in 1,5 M HCl with TPP/Pt ratio 4. Repeated scans after (a) 5 minutes (b) 15 minutes (c) 25 minutes (d) 50 minutes.

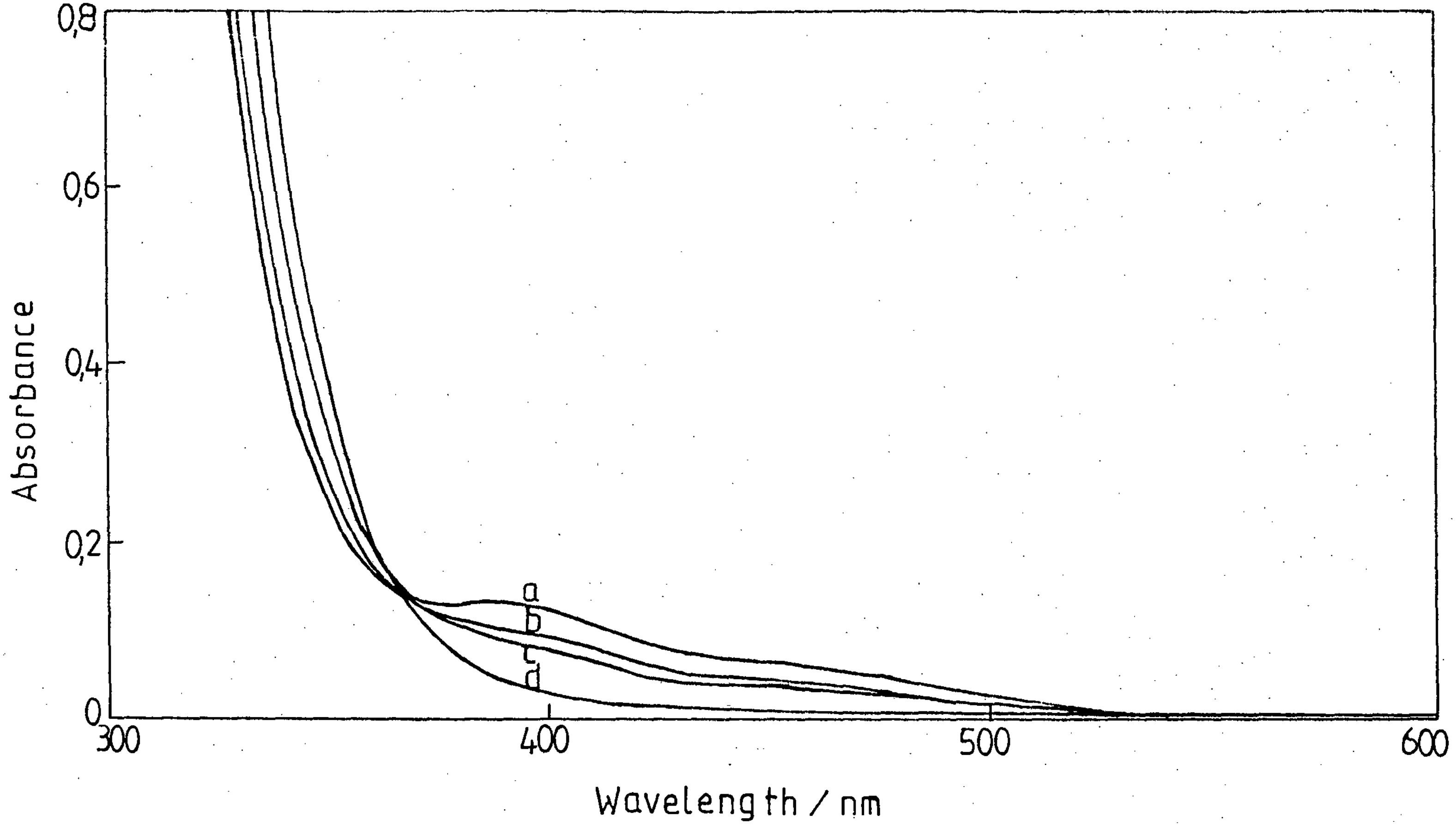


Figure 3.6(ii) Sn(II)/Pt(II) ratio 2 in 1,5 M HCl with TPP/Pt ratio 1. Repeated scans (a)-(d) after same time intervals as Figure 3.6(i).

3.2 The Effect of Time

Mojski [44] chose to perform his extractions with a 60 minute shaking period for aqueous phases not containing stannous chloride and for 10 minutes when tin(II) had been added. He appears to have chosen these times at random, assuming equilibrium to have been reached after this period.

As described in Section 3.1, it was necessary to initially allow sufficient time for equilibration of the aqueous phases before carrying out an extraction. Preliminary studies also showed that the amount of metal extracted varied with time of shaking, according to the particular Pt(II)/Sn(II) and Pt(II)/TPP ratios. It was therefore necessary to undertake a detailed study of the effect of time on the extraction instead of assuming a definite shaking period.

Experiments were carried out by pre-equilibrating the platinum-tin phase followed by shaking for various times with an equal volume of dichloromethane containing TPP. The percentage metal extracted was determined from atomic absorption measurements and comparison with a blank.

Figures 3.7 and 3.8 show that the percentage metal extraction does in fact change with time. In general, for a particular Pt/PPh_3 ratio, the percentage extraction of platinum increases with time, whereas tin(II) extraction initially increases but over a long period drops dramatically. We therefore decided that it was necessary to examine the effect of time throughout our experiments since it was evident that the extraction varied quite dramatically with the period of shaking.

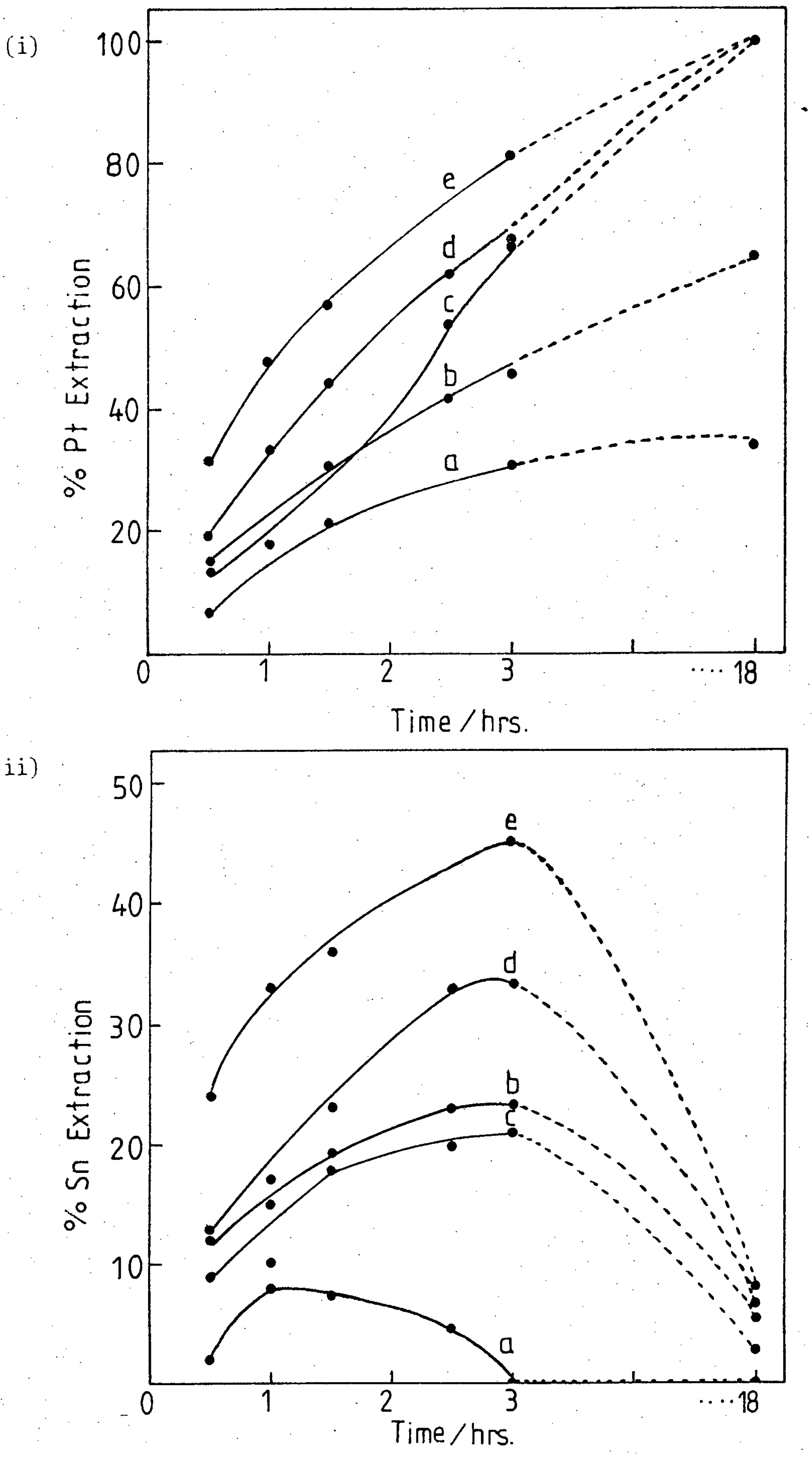
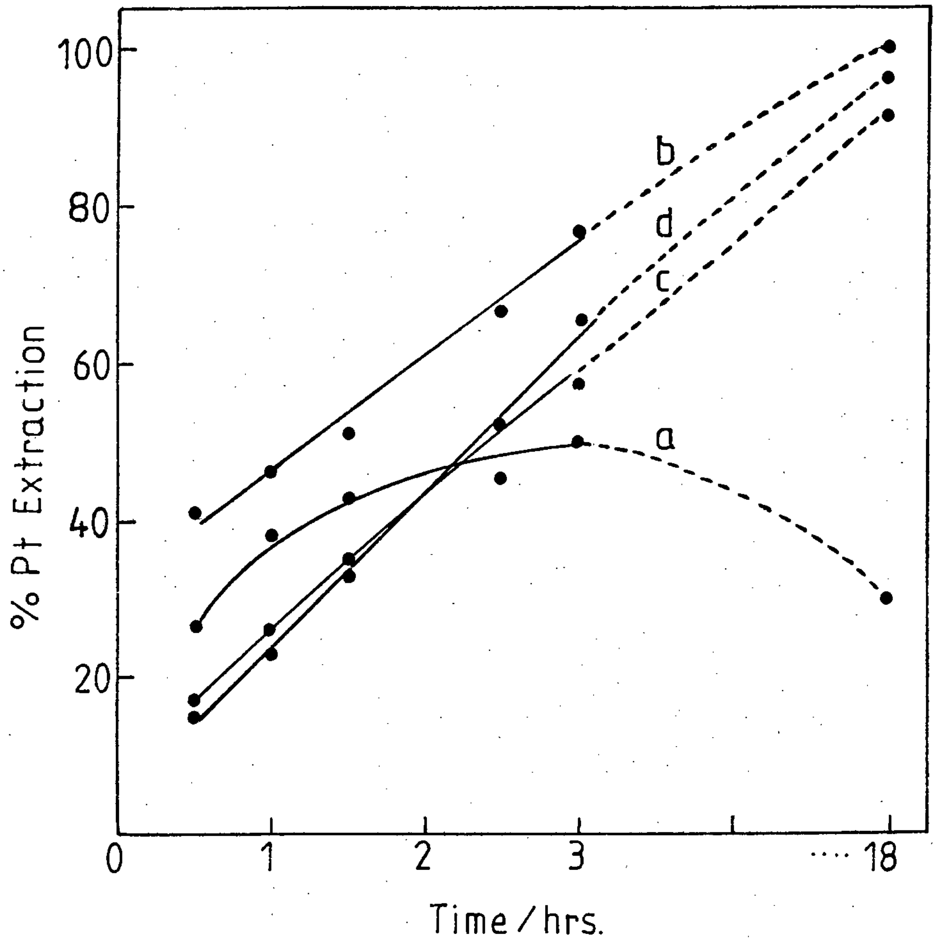


Figure 3.7 The variation of percentage extraction of (i) platinum (ii) tin with time at 1 M HCl, a Sn(II)/Pt(II) ratio of 2 and PPh_3/Pt ratios of (a) 1 (b) 2 (c) 4 (d) 6 and (e) 10.

(i)



(ii)

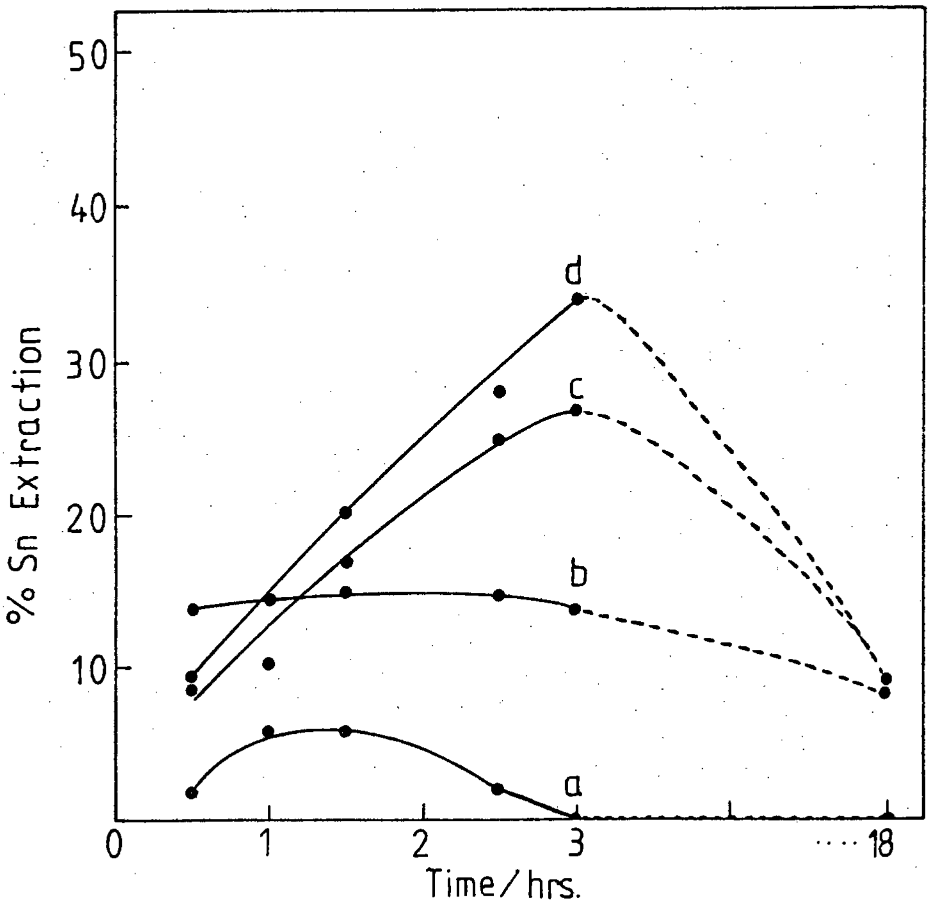


Figure 3.8 The variation of percentage extraction of (i) platinum (ii) tin with time at 1,5 M HCl, Sn(II)/Pt(II) ratio of 2 and PPh_3/Pt ratio of: (a) 1 (b) 2 (c) 4 (d) 10.

3.3 The Effect of Platinum : Triphenylphosphine Ratio

Preliminary qualitative extraction experiments showed that the apparent amount of platinum(II) extracted from a red solution containing Pt(II) and Sn(II) in the ratio of 1:2 in 1,5 M HCl medium depends on the relative quantity of TPP in the dichloromethane phase. Thus, the intensity of the red colour in the aqueous phase changes from its original value (no TPP present in the CH_2Cl_2 layer) to a pale yellow (TPP/Pt(II) ratio of *ca* 5) to almost colourless (TPP/Pt(II) ratio > 10). Mojski [44] used a large excess of TPP in his experiments (TPP/Pt ratio > 100) which results in very rapid removal of the red colour in the aqueous phase. Our preliminary experiments also showed that at TPP/Pt ratios of less than 10, the organic phase becomes coloured (from pale yellow to orange), suggesting the existence of a tin-containing platinum-phosphine complex. (Authentic samples of the prepared complex *cis*-$[Pt(PPh_3)_2(SnCl_3)Cl]$ are yellow-orange whereas the *trans*-isomer is white [45]).

Extraction experiments were performed as described in Section 3.2, varying the Pt(II)/TPP ratio from 1 to 10. Figures 3.9 and 3.10 show how the percentage metal extraction varies with Pt(II)/TPP ratio at 1,0 and 1,5 M HCl concentrations.

A number of interesting observations may be made from these results. From Figures 3.9(i) and 3.10(i) it appears that the ratio of $PPh_3/Pt = 2$ is definitely of significance. At this value with 1,5 M HCl solutions there is a dramatic increase in percentage extraction of platinum from ½ - 3 hours of shaking. This seems to indicate that a complex containing Pt and TPP in the ratio of 1:2 might well be favoured in the organic phase,

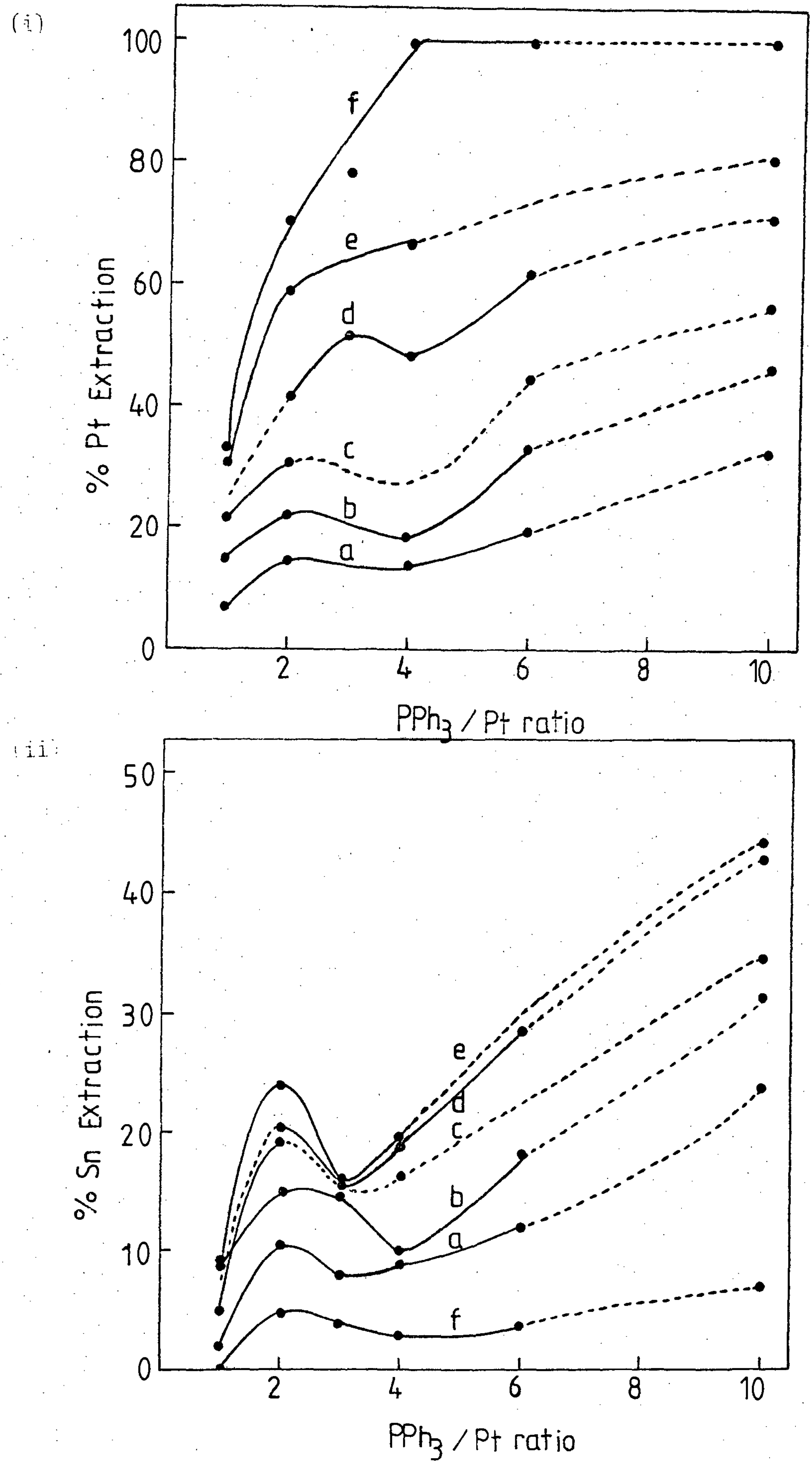


Figure 3.9 The variation of percentage extraction of (i) platinum (ii) tin from 1 M HCl solutions of Sn(II)/Pt(II) ratio 2 with TPP/Pt ratio after extraction times of: (a) ½ hr. (b) 1 hr. (c) 1½ hrs. (d) 2½ hrs. (e) 3 hrs. (f) 18 hrs.

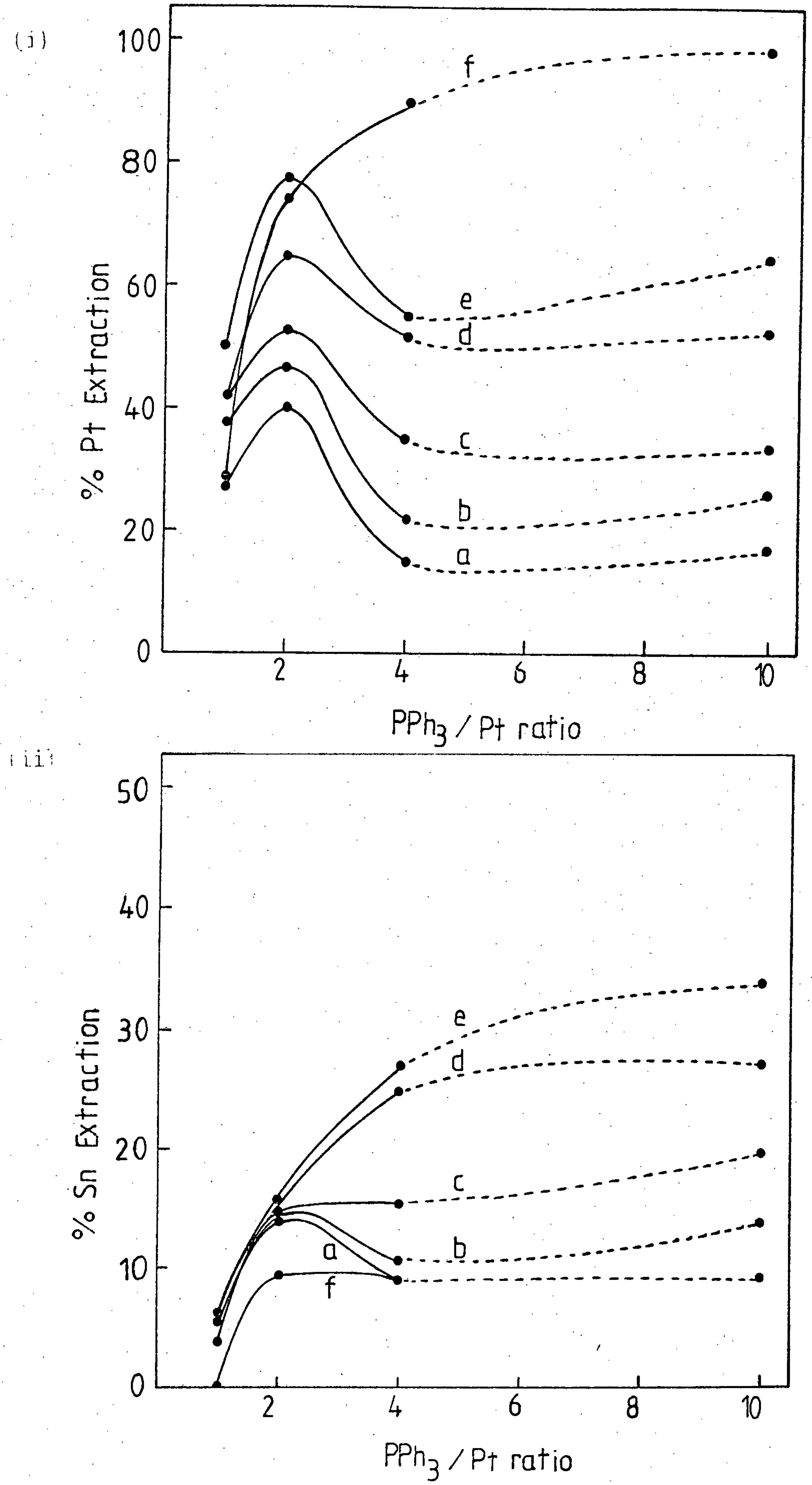


Figure 3.10 The variation of percentage extraction of (i) platinum (ii) tin from 1,5 M HCl solutions of Sn(II)/Pt(II) ratio 2 with TPP/Pt ratio after extraction times of: (a) ½ hr. (b) 1 hr. (c) 1½ hrs. (d) 2½ hrs. (e) 3 hrs. (f) 18 hrs.

resulting in rapid extraction under these conditions. A similar effect, although less pronounced, may be observed in solutions of 1M HCl. The more general trend at this acid concentration however appears to be an increase in percentage platinum extraction with increasing PPh_3/Pt ratio and time.

Figure 3.9(ii) and 3.10(ii) show that tin is in fact extracted into the organic phase, in some cases as much as 45%. The amount extracted increases with time up to 3 hours but on prolonged shaking (18 hours) there is a dramatic drop in the percentage extraction. The colour intensity of the CH_2Cl_2 layers was noted to increase with time from yellow to orange but after 18 hours the colour faded to become very pale yellow or colourless. This suggests the initial formation of Pt-Sn-phosphine complexes in the organic phase, which with time disproportionate to a platinum-phosphine complex and $SnCl_3^-$, the latter of which is extracted back into the aqueous phase.

The percentage tin extracted shows a general increase with increasing PPh_3/Pt ratios. This is in direct agreement with the observed colour intensities of the organic phases. At higher PPh_3 ratios, the colours are generally more intense, increasing from orange to a very dark red-orange and then fading as described previously on prolonged shaking. At lower PPh_3/Pt ratios however, the organic phases increase from very pale yellow to orange, again fading with time.

We may therefore conclude that after prolonged shaking platinum is almost completely extracted above a PPh_3/Pt ratio of 4. A PPh_3/Pt ratio of 2 results in a relatively high percentage platinum extraction between ½ and 3 hours of shaking, an effect which is particularly evident with 1,5 M HCl aqueous solutions. The amount of tin extracted generally increases with increasing PPh_3/Pt ratio and time up to 3 hours but with prolonged shaking the tin is back-extracted into the aqueous phase.

3.4 The Effect of Platinum(II) : Tin(II) Ratio

In the extraction studies described by Mojski [44], a large excess of stannous chloride was used. No attempt was made to protect the solutions from the atmosphere and in some cases the aqueous layers were boiled before extraction. Thus, although the molarity of the prepared tin(II) solution was 100 times greater than that of the platinum, the exact Sn(II)/Pt(II) ratio was not known.

We considered it important to study the effect of the tin(II) concentration on the extraction process. In order to perform experiments at a fixed Sn(II)/Pt(II) ratio, extreme care had to be taken to prevent oxidation of the tin(II) species. All solutions were freshly-prepared in nitrogen-saturated solvents and the extraction flasks, previously flushed with nitrogen, were securely stoppered to exclude traces of oxygen. Such a procedure is obviously difficult and tedious experimentally and, although a number of problems were encountered initially, final results obtained have provided some useful information regarding the effect of the Sn(II)/Pt(II) ratio.

Experiments were performed by equilibrating equal volumes of the two metal solutions, the appropriate tin(II) and platinum(II) concentrations having been chosen for each particular ratio. Solutions were shaken with the organic phase for various time periods and the percentage metal extracted was determined by atomic absorption and comparison with a blank. Figure 3.11 shows the results of a set of experiments at 1 M HCl and a PPh_3/Pt ratio of 2. Results from Figure 3.11 show that in the absence of tin, i.e. at a Sn/Pt ratio of 0, the percentage extraction of platinum is very low, in fact less than 10% after 3 hours of shaking. The diagram also clearly shows how the presence of stannous chloride dramatically increases the percentage Pt extracted.

Some interesting trends may be noted from these results. It is evident that the percentage extraction of Pt increases significantly at Sn(II)/Pt(II) ratio of 1, dropping off slightly at ratio 2 before increasing again at a ratio of 5. This trend suggests that, although the largest Sn/Pt ratio gave the highest percentage Pt extraction, a complex containing Pt:Sn in the ratio of 1:1 is a favourable species for the extraction process.

Figure 3.11(ii) shows that at a Sn/Pt ratio of 1, there is also a general increase in the amount of tin extracted, which drops off at higher ratios. The percentage of tin extracted increases gradually up to 2½ hours of shaking but decreases after 3 hours and is negligible after 18 hours. The colour of the organic phases was observed to parallel this trend. The CH_2Cl_2 layer was initially a pale yellow which developed to a darker orange with a longer shaking period. On prolonged extraction the organic phase faded to become almost

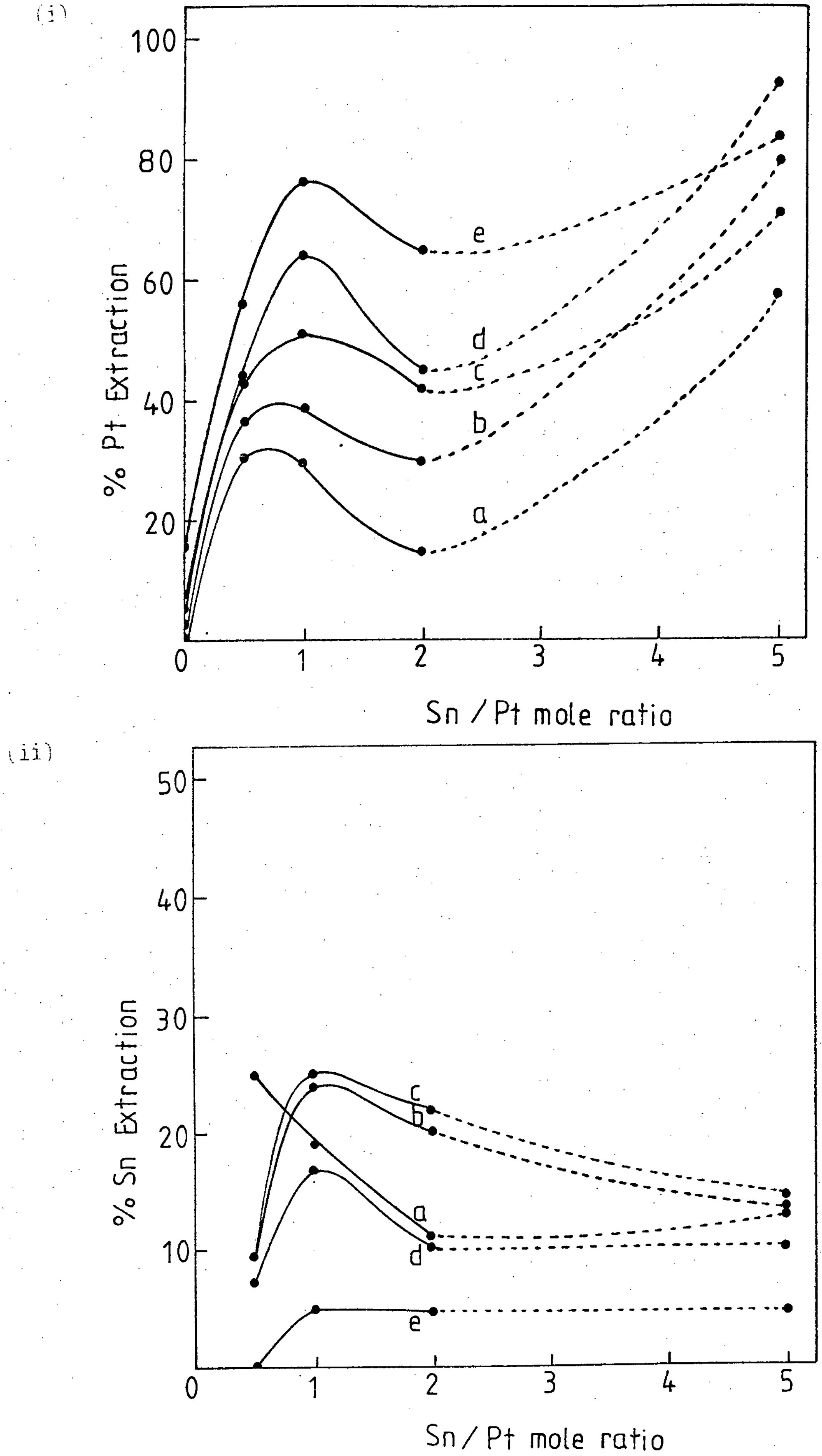


Figure 3.11 The variation of percentage extraction of (i) platinum (ii) tin from 1 M HCl solutions of PPh_3/Pt ratio 2 with Sn(II)/Pt(II) ratio after following times of extraction: (a) ½ hr.. (b) 1½ hrs. (c) 2½ hrs. (d) 3 hrs. (e) 18 hrs.

colourless. This is also in agreement with trends described in Sections 3.2 and 3.3.

From our studies on the effect of tin(II) at ratios of Sn(II)/Pt(II) between 0 and 5, we may therefore conclude that the highest ratio gave the largest percentages of platinum extraction for a particular period of shaking. However, a Sn(II)/Pt(II) ratio of 1 was found to give unusually high values for the amount of Pt extracted, suggesting that a Pt-Sn complex of this ratio is favoured in the extraction process. The percentage extraction of tin was also found to be high at Pt(II)/Sn(II) ratio of one.

3.5 The Effect of Hydrochloric Acid Concentration

Mojski [44] showed that platinum was completely extracted for all hydrochloric acid concentrations between 1 M and 6 M using large excesses of both tin(II) chloride and triphenylphosphine (Figure 1.2). We were interested to investigate in more detail the effect of acid concentration on the extraction process taking precautions to exclude air at all times. However, as evident from Section 3.1.1, we were only able to study conveniently extractions at acid concentrations from 1 - 1,5 M HCl.

Results showed that slight variations in the acid concentration in fact affected the extraction quite significantly. Initial equilibration times of the aqueous phases were more rapid in the case of solutions at 1 M HCl (10 minutes) than at 1,5 M HCl (20 minutes) (see Section 3.1.1). Figures 3.9 and 3.10 show that at 1,5 M HCl there is a dramatic increase in percentage Pt extraction at Sn(II)/Pt(II) ratio of 2, an effect which is far less pronounced in 1 M HCl solutions. It is also interesting to note that the amount of Pt extracted at higher TPP/Pt ratios is generally greater when using aqueous solutions of 1 M HCl.

However, it was evident that before we could draw any conclusions regarding the effect of HCl on the extraction process, a more thorough investigation at a range of other acid concentrations would be necessary. It was thus unfortunate that, due to the unavoidable problems of hydrolysis at lower acidities and oxidation by air at higher acid strengths, we were unable to work outside the acid concentration range of 1 - 1,5 M.

3.6 Studies with Prepared Platinum-Tin Complexes

In order to shed more light on the subject of complex formation in the CH_2Cl_2 phase, the *cis*- and *trans*-isomers $PtCl(SnCl_3)(PPh_3)_2$ and the compound *cis*-$PtCl_2(PPh_3)_2$ were prepared [45]. We believed that these complexes were formed at some stage during the extraction processes and that studies with the actual compounds might provide useful information about the mechanism of the extraction. Experiments were therefore carried out to ascertain whether a reaction of the following type, could be involved in the extraction mechanism:

$$\begin{array}{l} \textit{cis-} \\ \text{or} \\ \textit{trans-} \end{array} [PtCl(SnCl_3)(PPh_3)_2]_{org} + HCl \rightleftarrows$$

$$\begin{array}{l} \textit{cis-} \\ \text{or} \\ \textit{trans-} \end{array} [PtCl_2(PPh_3)_2]_{org} + [SnCl_3]^-_{aq} + H^+$$

Dichloromethane solutions of the *cis*- and *trans*-isomers of $PtCl(SnCl_3)(PPh_3)_2$ were shaken for 3 hours with portions of hydrochloric acid of various concentrations to determine whether the tin was back-extracted into the aqueous phase. Results in Table 3.2 obtained from atomic absorption spectroscopy show that, in the case of the *cis*-isomer, there is a general increase in percentage back-extraction of tin with increasing acid concentration. The *trans*-isomer appears to dissociate more readily for all acid concentrations in the range of 0,5 - 2,0 M hydrochloric acid, than the corresponding *cis*-isomer.

Acid concentration/ M	*cis*-isomer/ % back-extraction	*trans*-isomer / % back-extraction
0,5	83	96
1,0	90	100
1,5	79 [b]	100
2,0	95	100

[b] Could be subject to error

Table 3.2 Percentage back-extraction of tin from CH_2Cl_2 solutions of the *cis*- and *trans*-isomers of $PtCl(SnCl_3)(PPh_3)_2$ into aqueous HCl solutions.

An experiment was also performed to determine whether a dichloromethane solution of $PtCl_2(PPh_3)_2$ would extract tin from a 1 M HCl solution of stannous chloride. Results showed that on shaking for 18 hours approximately 12 % of the tin was extracted into the organic phase.

The above experiments therefore proved to be most useful since we confirmed that tin could in fact be back-extracted from an organic phase containing a Pt-Sn phosphine complex, into an aqueous acid phase. We were also able to show that the reverse reaction, i.e. the extraction of Sn from an $SnCl_2$ acid phase into a CH_2Cl_2 phase containing $PtCl_2(PPh_3)_2$, was possible.

3.8 Isolation of Complexes from the Organic Phase

Compounds were isolated from various organic phases in order to determine whether species such as $PtCl(SnCl_3)(PPh_3)_2$ and $PtCl_2(PPh_3)_2$ are formed during the extraction process.

After separation of the CH_2Cl_2 extracts from the aqueous layers, the organic solvent was removed by evaporation and infrared spectroscopy was used for the characterisation of the yellow to orange-red residues. By careful separation techniques, it was possible to obtain characterisable complexes from some of the residues. The infrared spectra of prepared complexes and the isolated species are shown in Figures 3.12 - 3.16. Detailed values of the absorption maxima are reported in Table 3.3. Results obtained appear to be in approximate agreement with the reported literature values for these compounds [45,81,82].

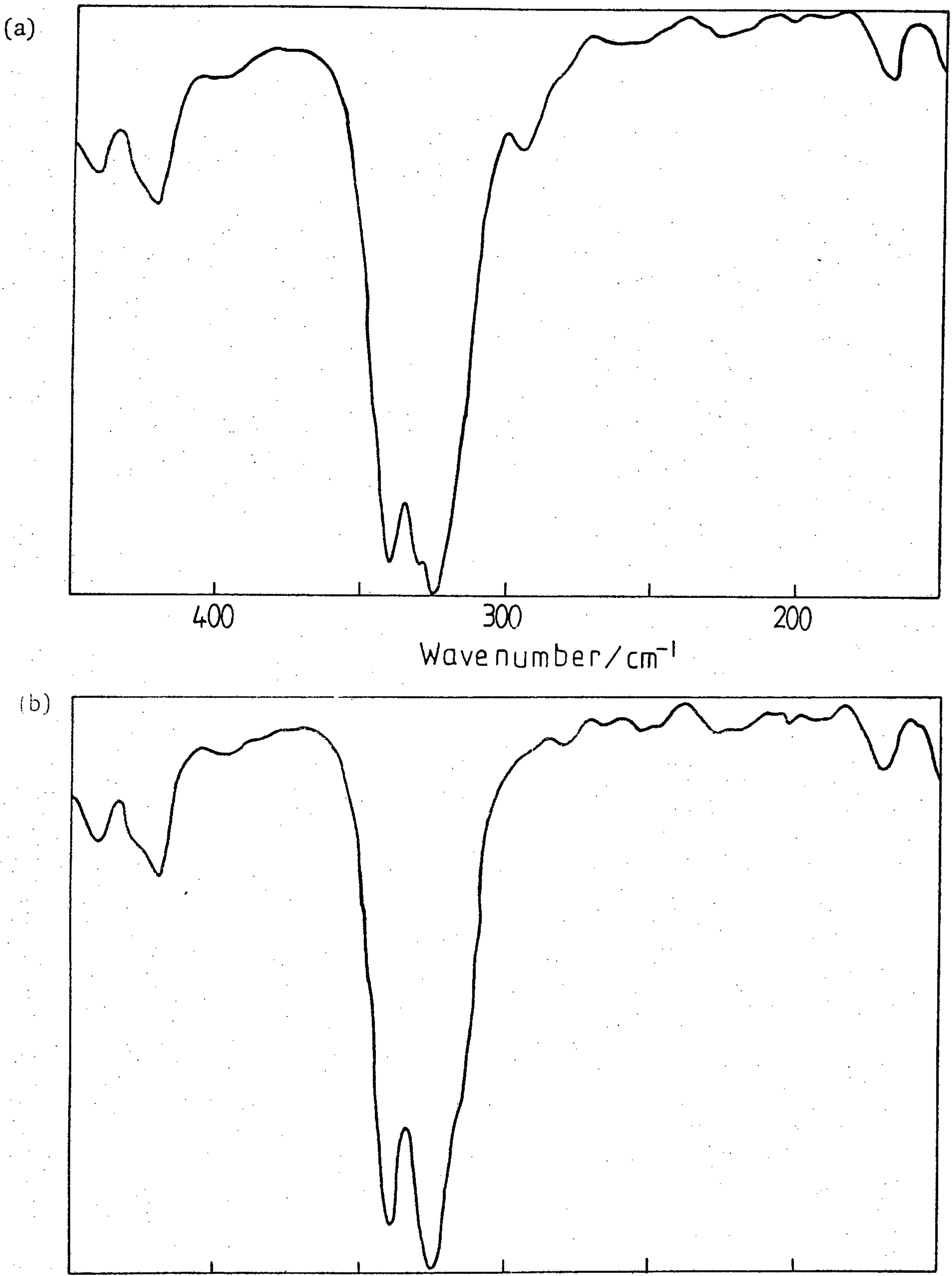


Figure 3.12 Infrared spectrum of (a) *cis*-[PtCl(SnCl$_3$)(PPh$_3$)$_2$] and (b) *trans*-[PtCl(SnCl$_3$)(PPh$_3$)$_2$].

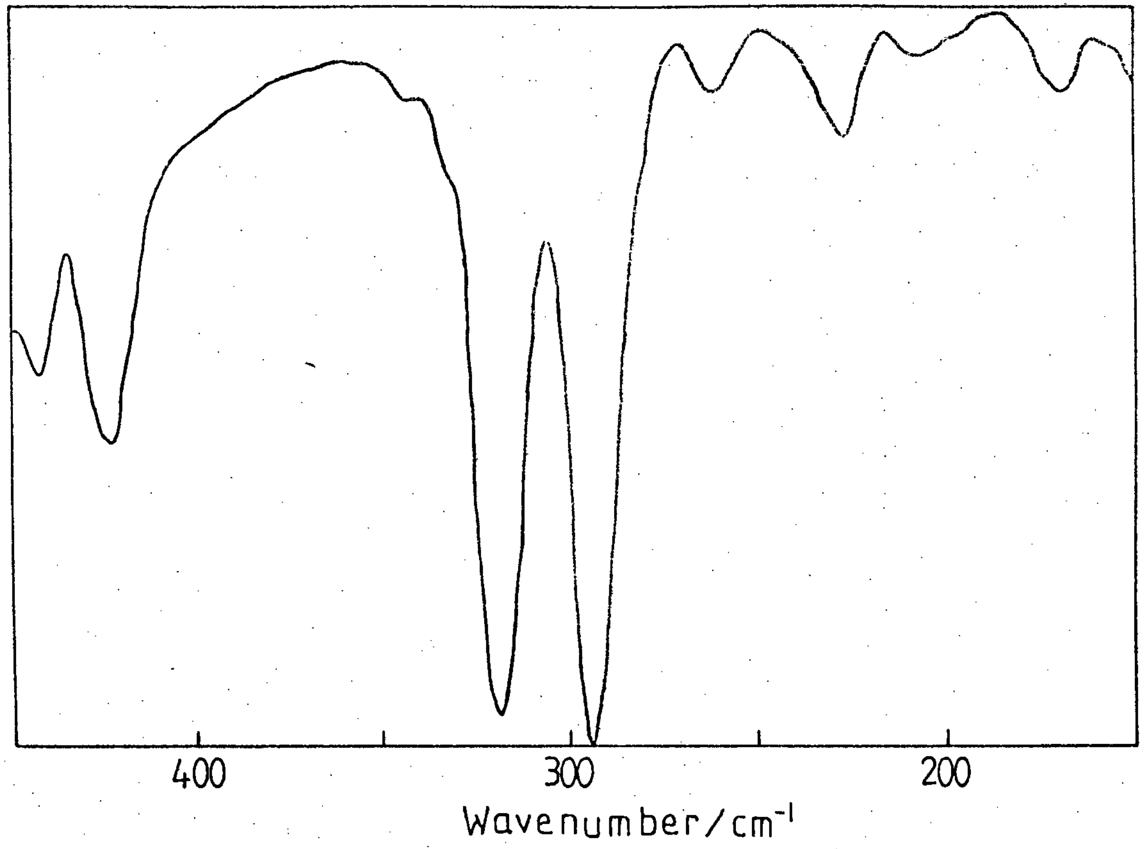


Figure 3.13 Infrared spectrum of *cis*-[$PtCl_2(PPh_3)_2$]

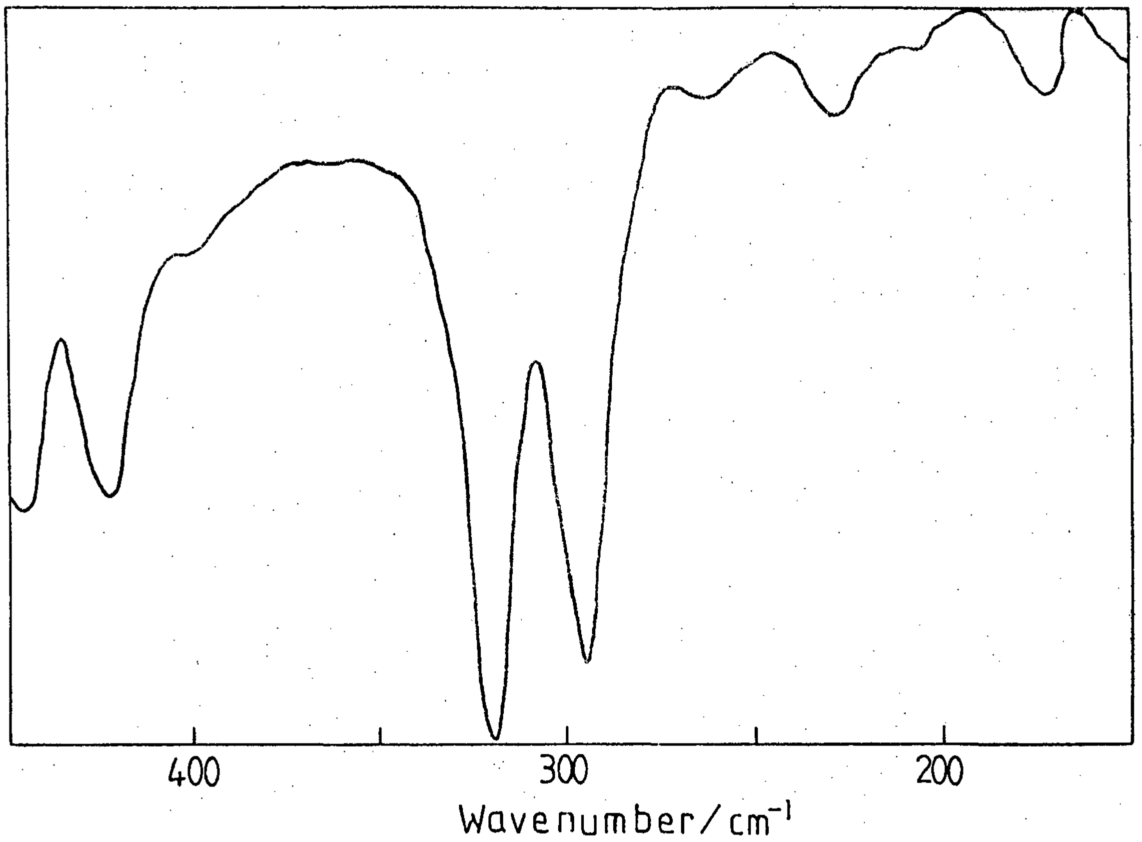


Figure 3.14 Infrared spectrum of compound isolated from organic residue after extraction for 8 hours. Conditions: 1,5 M HCl, Sn(II)/Pt(II) ratio 2, PPh_3/Pt(II) ratio 2.

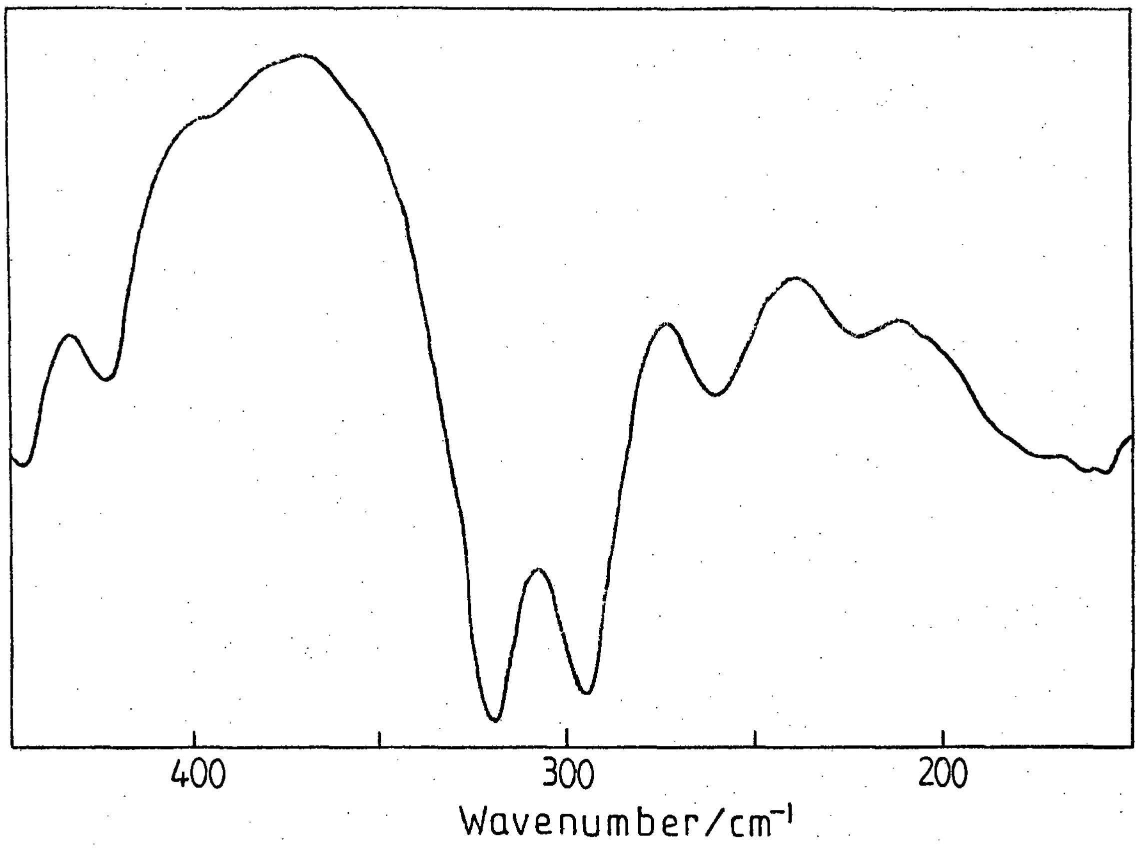


Figure 3.15 Infrared spectrum of organic residue after extraction for 18 hours. Conditions: 1 M HCl, Sn(II)/Pt(II) ratio 2, PPh_3/Pt(II) ratio 2.

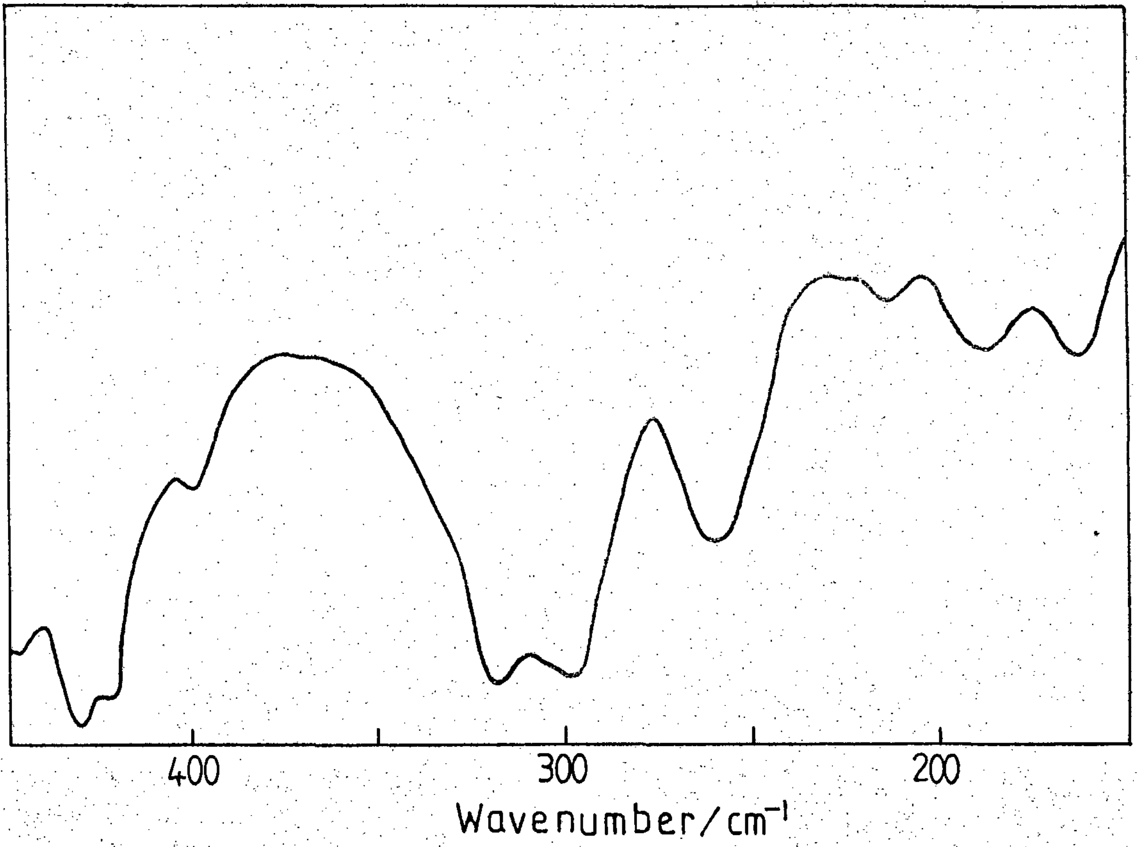


Figure 3.16 Infrared spectrum of organic residue after extraction for 3 hours. Conditions: 1 M HCl, Sn(II)/Pt(II) ratio 2, PPh_3/Pt(II) ratio 10.

Complex	Figure reference to infrared diagram	Absorption maxima / cm^{-1}
cis-$PtCl(SnCl_3)(PPh_3)_2$	3.12a	442(vw), 421(w), 340(s), 330(sh), 324(vs), 295(vw).
trans-$PtCl(SnCl_3)(PPh_3)_2$	3.12b	441(vw), 420(w), 340(s), 326(vs)
cis-$PtCl_2(PPh_3)_2$	3.13	442(vw), 422(w), 318(s), 294(vs), 261(vw), 227(vw)
Residue 1	3.14	446(w), 442(w), 320(vs), 295(s)
Residue 2	3.15	446(m), 424(w), 320(vs), 295(s), 260(w)
Residue 3	3.16	430(vs), 422(s), 399(w), 317(s), 296(s), 260(m)

Table 3.3 Infrared data for the complexes illustrated in Figures 3.12 - 3.16.

Comparison of Figures 3.14 and 3.15 with Figure 3.13 shows that the complex $PtCl_2(PPh_3)_2$ is present in these particular organic phases. The sample obtained for Figure 3.14 was separated from the organic residue and microanalytical data for the compound was found to agree with that for $PtCl_2(PPh_3)_2$. Organic residues from various other extractions were also found to contain $PtCl_2(PPh_3)_2$.

Figure 3.16 is a somewhat more complicated spectrum. $PtCl_2(PPh_3)_2$ appears to be the chief product although there is some broadening in the area 325 - 340 cm^{-1} which suggests the presence of one or both of the isomers of $PtCl(SnCl_3)(PPh_3)_2$. The percentage extraction of tin determined by atomic absorption for this particular experiment was about 45%, which further supports the existence of a tin-containing complex in the organic phase.

The above results prove the existence of $PtCl_2(PPh_3)_2$ in the organic phase and evidence exists that $PtCl(SnCl_3)(PPh_3)_2$ is also formed in this phase.

CHAPTER 4

CHAPTER 4

4. DISCUSSION AND CONCLUSION

Results of our studies on the extraction of platinum from stannous chloride solutions using triphenylphosphine have provided useful information regarding the mechanisms involved in such processes. The extraction was in fact found to be extremely complicated and was affected quite dramatically by traces of oxygen. This meant that the strictest precautions had to be taken to exclude air at all times which resulted in great difficulties experimentally. However, on the basis of our final results, we are now able to propose a reasonable mechanism for the extraction process.

It is known that a number of species are formed when stannous chloride is prepared in hydrochloric acid medium. Figure 4.1 shows a plot of the various complexes as a function of the chloride concentration obtained using the program 'Pseudoplot', an extended Fortran version of 'Haltafall' [83]. Stability constants were obtained from Smith and Martell [84].

The distribution of the species in hydrochloric acid solutions of K_2PtCl_4 as a function of chloride concentration was also calculated. Data from work by Elding was used in the 'Pseudoplot' program [85,86]. $[PtCl_4]^{2-}$ was shown to be the dominant species from 0,5 - 1,5 M chloride concentrations, with negligible amounts of $[PtCl_3(H_2O)]^-$ and $[PtCl_2(H_2O)_2]$ also present.

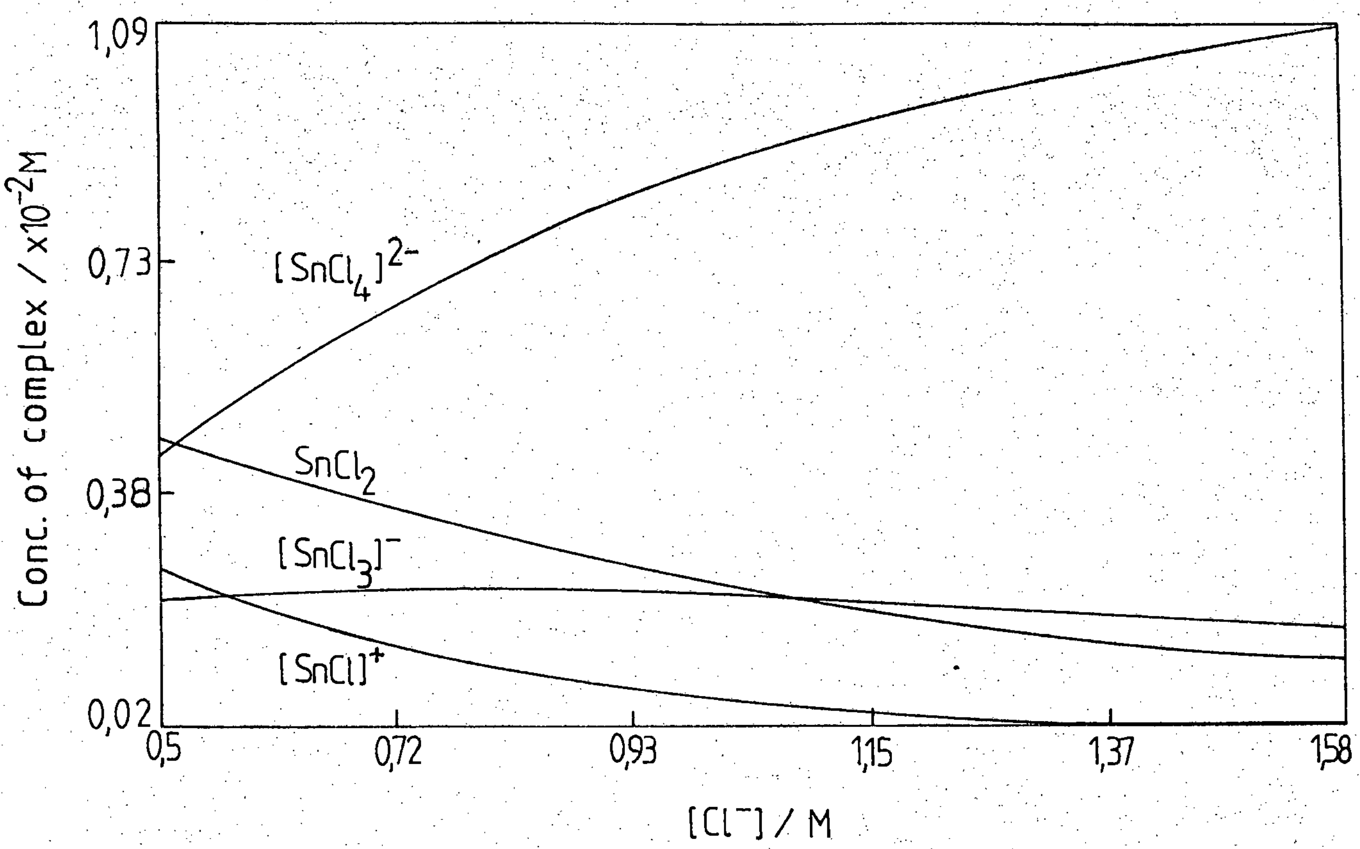


Figure 4.1 The distribution of tin(II) chloride complexes as a function of chloride concentration

Thus, due to the number of different complexes formed in acidic platinum and tin solutions, it is obvious that, on mixing, an extremely complicated series of reactions will occur. Examples of some of the species which are likely to be formed in equilibrium with each other are:

$SnCl_4^{2-} \rightleftarrows SnCl_3^- + Cl^-$
$SnCl_2 + Cl^- \rightleftarrows SnCl_3^-$
$PtCl_4^{2-} + SnCl_3^- \rightleftarrows [Pt(SnCl_3)Cl_3]^{2-} + Cl^-$
$[Pt(SnCl_3)Cl_3]^{2-} + SnCl_3^- \rightleftarrows$ *cis*- or *trans*-$[Pt(SnCl_3)_2Cl_2]^{2-} + Cl^-$
cis- or *trans*-$[Pt(SnCl_3)_2Cl_2]^{2-} + SnCl_3^- \rightleftarrows [Pt(SnCl_3)_3Cl]^{2-} + Cl^-$
cis- or *trans*-$[Pt(SnCl_3)_2Cl_2]^{2-} + 3SnCl_3^- \rightleftarrows [Pt(SnCl_3)_5]^{3-} + 2Cl^-$

Such processes are presumably relatively slow since a period of 10 - 20 minutes was necessary for mixed Pt and Sn solutions to reach equilibrium as measured by the constancy of the absorbance spectra. The length of time required varied according to the molarity of the acid, a fact which could be explained by the differences in the distribution of the tin species with Cl^- concentration (see Figure 4.1).

The extraction process is further complicated by the presence of triphenylphosphine in the organic phase. A number of possible complexes could be formed in both phases which may be represented by the following equilibria,

(1) $[PtCl_4]^{2-}_{aq} + [PPh_3]_{org} \rightleftarrows [PtCl_3(PPh_3)]^-_{aq} + Cl^-_{aq}$

(2) $[PtCl_3(PPh_3)]^-_{aq} + [PPh_3]_{org} \rightleftarrows [PtCl_2(PPh_3)_2]_{org} + Cl^-_{aq}$

(3) $[Pt(SnCl_3)Cl_3]^{2-}_{aq} + [PPh_3]_{org} \rightleftarrows [Pt(SnCl_3)Cl_2(PPh_3)]^-_{aq} + Cl^-_{aq}$

(4) $[Pt(SnCl_3)Cl_3]^{2-}_{aq} + [PPh_3]_{org} \rightleftarrows [Pt(PPh_3)Cl_3]^-_{aq} + [SnCl_3]^-_{aq}$

$$(5)\quad [Pt(SnCl_3)_2Cl_2]^{2-}_{aq} + [PPh_3]_{org} \rightleftarrows [Pt(SnCl_3)_2Cl(PPh_3)]^{-}_{aq} + Cl^{-}_{aq}$$

$$(6)\quad [Pt(SnCl_3)_2Cl_2]^{2-}_{aq} + [PPh_3]_{org} \rightleftarrows [Pt(SnCl_3)Cl(PPh_3)]^{-}_{aq} + [SnCl_3]^{-}_{aq}$$

$$(7)\quad [Pt(SnCl_3)Cl_2(PPh_3)]^{-}_{aq} + [PPh_3]_{org} \rightleftarrows [Pt(SnCl_3)Cl(PPh_3)_2]_{org} + Cl^{-}_{aq}$$

$$(8)\quad [Pt(SnCl_3)Cl_2(PPh_3)]^{-}_{aq} + [PPh_3]_{org} \rightleftarrows [PtCl_2(PPh_3)_2]_{org} + [SnCl_3]^{-}_{aq}$$

$$(9)\quad [Pt(SnCl_3)Cl(PPh_3)_2]_{org} + [PPh_3]_{org} \rightleftarrows [PtCl_2(PPh_3)_2]_{org} + [SnCl_3]^{-}_{aq}$$

Experiments showed that the percentage Pt extracted was dependent on the amount of triphenylphosphine in the dichloromethane phase. A significant increase in the percentage extraction of platinum was observed at a PPh_3/Pt ratio of 2, suggesting that a platinum-phosphine complex of this ratio was favoured in the organic phase (Figures 3.9 and 3.10). Results also showed that there was a dramatic increase in percentage extraction of platinum and tin at a Pt(II)/Sn(II) ratio of 1, which indicated the favourable formation of a 1:1 Pt-Sn complex in the CH_2Cl_2 phase. (Figure 3.11). Tin was found to be extracted back into the aqueous phase with time, which provided evidence for the disproportionation of the Pt-Sn complex with prolonged shaking.

We therefore propose that the chief complexes existing in the organic phase after extraction are the platinum-phosphine compounds, $PtCl(SnCl_3)(PPh_3)_2$ and $PtCl_2(PPh_3)_2$. Experimental evidence supports the initial formation of $PtCl(SnCl_3)(PPh_3)_2$ in the CH_2Cl_2 layer which disproportionates to $PtCl_2(PPh_3)_2$ with concommitant back-extraction of tin into the aqueous phase.

The platinum-phosphine complexes $PtCl(SnCl_3)(PPh_3)_2$ and $PtCl_2(PPh_3)_2$ are known to exist [45]. Experiments carried out with these compounds provided further evidence in support of our proposed mechanism. Reaction (9) in the above equations showing formation of $PtCl_2(PPh_3)_2$ by disproportionation of $PtCl(SnCl_3)(PPh_3)_2$ would be favoured on increasing the chloride concentration. Treatment of *cis*-$[PtCl(SnCl_3)(PPh_3)_2]$ in CH_2Cl_2 with solutions of increasing hydrochloric acid strength showed that the back-extraction of tin increased with increasing chloride concentration. Studies with prepared $PtCl_2(PPh_3)_2$ also showed that this complex would extract tin from a 1 M hydrochloric acid solution, so confirming the possibility of the reverse process of equation (9).

It is also interesting to note that Young [19] isolated the complex $PtCl(SnCl_3)(PPh_3)_2$ from ethanolic platinum-tin solutions and found that it disproportionates in acetone to give $PtCl_2(PPh_3)_2$. The latter complex dissolved in acetone containing excess tin(II) chloride to reform the Pt-Sn compound, which suggested the existence of the equilibrium:

$$[PtCl(SnCl_3)(PPh_3)_2] + \text{acetone} \rightleftarrows [PtCl_2(PPh_3)_2] + SnCl_2(\text{acetone})$$

Infrared spectroscopy confirmed the presence of $PtCl_2(PPh_3)_2$ in the organic phase and although evidence was not conclusive, it appeared that some $[PtCl(SnCl_3)(PPh_3)_2]$ was also formed.

To conclude, we have therefore confirmed that the presence of stannous chloride dramatically increases the extraction of platinum from aqueous HCl solutions of K_2PtCl_4 into dichloromethane containing triphenylphosphine.

Suitable analytical methods were devised for the determination of metal concentrations in the extractions which provided a means of studying the system in detail. Results showed that the amount of platinum and tin extracted was dependent on the time period of extraction, the Pt(II)/PPh_3 and Pt(II)/Sn(II) ratios as well as the HCl concentration. Detailed studies on the effect of these various conditions allowed us to postulate a model for the extraction system.

It is now evident that in systems of this kind both platinum and tin are initially extracted into the organic phase, almost certainly complexed as $PtCl(SnCl_3)(PPh_3)_2$. With time this species dissociates to $PtCl_2(PPh_3)_2$ in which form the platinum remains in the organic phase and the tin is extracted back into the aqueous layer. Since it is unlikely that significant differences would have resulted by using dichloromethane instead of dichloroethane, we have shown that Mojski's [44] description of tin as a 'labilizing agent' in the extraction of platinum by triphenylphosphine was in fact an oversimplification.

CHAPTER 5

CHAPTER 5

5. EXPERIMENTAL

5.1 Chemicals, Reagents and Glassware

Commercial grade nitrogen supplied by Afrox, Cape Town was used throughout. The gas was purged of oxygen by passing it through a chromous chloride solution and distilled water before use [87].

Glass-distilled water saturated with nitrogen was used for all aqueous solutions. The water was initially boiled for twenty minutes to remove dissolved carbon dioxide and oxygen and allowed to cool under nitrogen. It was stored in a glass aspirator fitted with a nitrogen inlet.

Concentrated A.R. hydrochloric acid was degassed by passing nitrogen through the solution for fifteen minutes. The A.R. dichloromethane was refluxed for 30 minutes under nitrogen before use.

All chemicals and reagents were analytically pure and generally supplied by Merck, Darmstadt. K_2PtCl_4 was obtained from Johnson Matthey, Wadeville and $SnCl_2.2H_2O$ from Hopkin and Williams Ltd., England. The triphenylphosphine from Fluka AG, Germany, was found to be analytically pure. (Found: C, 82.2; H, 5.7 %. Calc. for $P(C_6H_5)_3$: C, 82.4; H, 5.8 %). Potassium iodate was dried for 1 hour at 100°C and stored in a desiccator. Stannous chloride standard solution for atomic absorption spectroscopy (1 ml ≈ 1,00 mg Sn) was supplied by BDH Chemicals, England.

Aqua regia was prepared from A.R. HNO_3 and HCl in the ratio 18:82 [88].

$La(NO_3)_3.xH_2O$ (where x is assumed to be 6) was prepared by dissolving La_2O_3 in A.R. HNO_3. The resulting clear solution was evaporated to dryness, distilled water was added with repeated evaporations to remove excess HNO_3. The final aqueous solution was filtered and then evaporated to leave a white solid.

The glassware was all of B grade, except for an A grade burette used in the determinations with potassium iodate. Pipettes and quartz spectrophotometric cells were stored in 10 % solutions of Contrad detergent. Piston burettes fitted with a nitrogen inlet were used to dispense the platinum and tin solutions. Dichloromethane solutions were delivered from a burette fitted with a Teflon tap and nitrogen inlet. Mettler and Sartorious four decimal balances were used for all weighings.

Microanalyses were performed on a Heraeus Universal Combustion Analyser, Model CHN-Micro, by Mr W.R.T. Hemsted of the Department of Organic Chemistry, University of Cape Town.

5.2 Atomic Absorption of Platinum

Platinum stock solutions of approximately 1200 p.p.m. (0,006 M) were prepared by dissolving K_2PtCl_4 in 1 M or 1,5 M hydrochloric acid. The copper sulphate used in the preliminary experiments was prepared as an

8 % aqueous stock solution and diluted accordingly. $La(NO_3)_3$ stock solution of 20 000 p.p.m. was made up at the required HCl concentration and diluted ten times on addition to the standards and samples, to give a final La^{3+} concentration of 0,2 %.

Sets of standards were prepared for platinum in 1 or 1,5 M HCl in the range of 1 - 150 p.p.m. with additions of tin in a ratio to match the sample matrix as closely as possible. Stannous chloride solutions of appropriate strength were made by dissolving the solid in concentrated HCl, warming gently and diluting with water. Both metal solutions were prepared freshly each day but in some cases were used the day after preparation.

A set of standards in *aqua regia* was also prepared for use in Pt determinations after ashing of the organic phase. Platinum metal was dissolved in about 15 % of *aqua regia* by warming gently and diluting with water to give a 1000 p.p.m. stock solution.

All samples were run within 3 days of preparation and standards were made freshly each time.

Table 5.1 shows the settings for the various atomic absorption spectrophotometers used. The Varian Techtron Models 1000 and AA6 were used in the preliminary experiments. The Perkin Elmer 5000 machine was used for all other measurements. Air-acetylene flames were strongly oxidising.

	Lamp current/ mA	Wavelength/ nm	Slit width/ nm	Burner height	Fuel flow/ ℓ min^{-1}	Support flow/ ℓ min^{-1}
Varian Techtron 1000	10	265,8	0,2	3,5	2,0*	6,5*
Varian Techtron AA6	10	265,9	0,2	7,5	0,5*	5,5*
Perkin Elmer 5000	10	265,9	0,2	4,0	1,6	22,5

* In machine scale units

Table 5.1 Settings for atomic absorption spectrophotometers.

Percentage extraction of platinum in each sample (error less than 2 %) was calculated from a blank value in the following way:

$$\frac{[\mathrm{Pt}]_B - [\mathrm{Pt}]_S}{[\mathrm{Pt}]_B} \times 100$$

where $[\mathrm{Pt}]_B$ = concentration of platinum in blank, and $[\mathrm{Pt}]_S$ = concentration of platinum in sample.

5.3 Atomic Absorption of Tin

Standard stock solutions of 1000 p.p.m. tin in 10 % HCl were prepared by dissolving the powdered metal in concentrated acid with gentle warming and diluting to volume with distilled water. Stock solutions were made up freshly every 3 weeks.

A series of standards was prepared in the range of 0 - 150 p.p.m. All samples were run in 10 % HCl, within 3 days of preparation. Standard stannous chloride solution of 1000 p.p.m. in 1 M HCl for atomic absorption spectroscopy was purchased half way through the project. Since the standard curve obtained compared favourably with the previous one, this stock solution was used for the rest of the work.

All measurements were made using a Perkin Elmer 5000 spectrophotometer with a strongly reducing flame and the following conditions:

Lamp current / mA	10
Wavelength / nm	286,3
Slit width / nm	0,7
Burner height	4
Fuel / ℓ min^{-1}	2
Support / ℓ min^{-1}	22

Percentage tin extraction in each sample (error less than 2 %) was calculated from a blank value in the following way:

$$\frac{[\mathrm{Sn}]_B - [\mathrm{Sn}]_S}{[\mathrm{Sn}]_B} \quad \times \quad 100$$

where $[\mathrm{Sn}]_B$ = concentration of tin in blank, and $[\mathrm{Sn}]_S$ = concentration of tin in sample.

5.4 Potassium Iodate Oxidations

The stannous chloride and K_2PtCl_4 solutions were prepared as described in Section 5.2. For the original investigations outlined in Section 2.3, tin(II) and platinum(II) solutions of 0,02 - 0,04 M and 0,01 - 0,02 M respectively, in 1,5 M HCl, were used.

Potassium iodate solutions of appropriate strengths were made by dissolving the dried solid in distilled water.

All titrations were performed under nitrogen using a titration flask fitted with a special bung (Figure 5.1). Standardisation of tin(II) solutions throughout the work was carried out according to the method of Vogel [64].

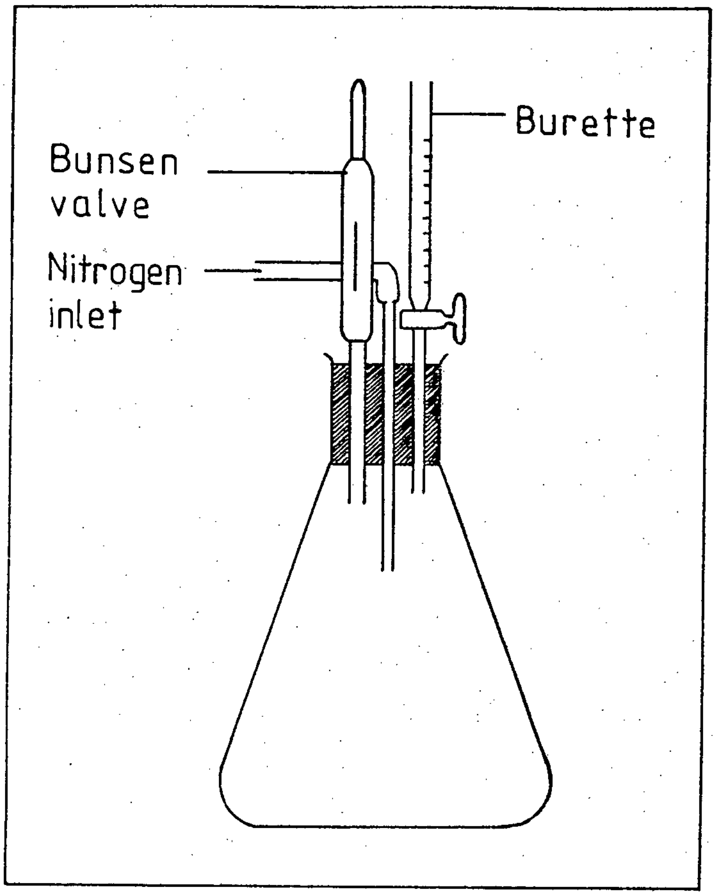


Figure 5.1 Flask with adapted bung for titrations under nitrogen.

For the titration of total tin(II) and platinum(II), portions containing 10 ml tin(II) solution, 5 ml platinum(II) solution, 15 ml concentrated HCl, 8 ml H_2O and 10 ml chloroform were transferred to the titration flask, previously flushed out with nitrogen. During addition of the potassium iodate, the aqueous solution underwent a number of colour changes. Initially the intense red colour faded and the solution became paler yellow but on addition of about 60 % of the required volume of iodate, the solution became red-brown and a dark precipitate formed at the interface of the organic and aqueous layers. This precipitate disappeared as more iodate was added. At this stage the solution was shaken well and left to stand for 3 - 4 minutes to allow the iodine colour to develop to maximum intensity. The titration was then continued slowly, shaking well after each addition of KIO_3, until the chloroform layer was no longer violet.

In the titration of a platinum(II) solution, a similar procedure was followed. 5 ml Pt(II) solution, 5 ml concentrated HCl, 8 ml water and 10 ml chloroform were used for each titration. On addition of the KIO_3, the aqueous layer turned a dark yellow which intensified gradually as more iodate was added. At this stage, when approximately 70 % of the required KIO_3 had been added, the solution was shaken well and allowed to stand for about 4 - 5 minutes with occasional shaking, to enable the violet colour to develop. The titration was continued as described previously, the dark yellow of the aqueous layer fading noticeably as the end point was approached.

Oxidation of only the tin(II) in solutions of platinum(II) and tin(II) was carried out in the following way. A filter flask containing the metal solutions was fitted with a rubber stopper and glass tube and air was bubbled through by water suction. A titration with KIO_3 to determine the Pt(II) remaining, was then performed as described previously. The experiment was repeated by bubbling pure oxygen through the solution instead of air.

5.5 Polarography

Stannous chloride and K_2PtCl_4 solutions of 0,0085 M and 0,0140 M respectively were prepared as described in Section 5.2. 0,5 g Gelatine was dissolved in 100 ml hot distilled water to give a 0,5 % gelatine solution.

A 25 ml portion of the tin solution and 1 ml of gelatine was pipetted into the solution vessel of the polarograph. One ml additions of Pt solution were made with a pipette to the mixture. Solutions were degassed for 15 minutes to remove dissolved oxygen, before the recording of a polarogram. Similar experiments were repeated with 4 M ammonium chloride as the supporting electrolyte. A new tin solution was prepared, also in 1 M HCl but containing 4 M ammonium chloride and 0,005 % gelatine for this purpose.

A Metrohm Polarecord with the following settings was used:

AC normal mode
$t_{drop} = 2$ s
$U_{start} = -0{,}2$ V
$\Delta U = -1$ V
AC x 0,1 = 10×10^{-7} A / mm
$t_{comp} = 1{,}35$
mm / t_{drop} = 0,5 mm
$U_n = 0{,}5$ m V
$f_K = 25$ Hz.

5.6 Ashing of the Organic Phase

The dichloromethane phase was carefully separated from the aqueous layer and transferred to a porcelain crucible. The solvent was removed by gentle warming and the solid was then ashed by heating vigorously to bright red glow for 5 minutes with a bunsen burner. One ml of *aqua regia* was added and the mixture was heated vigorously for a further 5 minutes.

The solution was transferred to a volumetric flask and made to volume with water and 0,2 % $La(NO_3)_3$. The mixture was then filtered to remove the insoluble black particles and the concentration of platinum was determined by atomic absorption.

5.7 Distillation of Tin

A typical distillation apparatus was used for the attempted analysis of tin in organic phase samples. The general procedure described by Onishi and Sandell was followed [75].

The organic phase portions were transferred to the distillation flask and the dichloromethane was evaporated with gentle warming of the solution. A small portion of 6 N hydrochloric acid was added to the residue. A 50 ml beaker containing 5 ml cold water was placed under the condenser as the receiving vessel. A mixture of 15 ml of 6 N HCl and 7 ml HBr was added drop by drop while maintaining the flask temperature between 150 and 160°C with an oil bath. Various times of distillation were investigated, from 15 - 45 minutes. The distillate was transferred to a volumetric flask and made to volume with 10 % HCl for determination by atomic absorption.

After reaction, portions of the starting solutions were removed and tested for the presence of tin by bubbling hydrogen sulphide gas through the solution [74]. A yellow precipitate indicated the presence of tin.

5.8 Solvent Extraction Procedures

The platinum and tin solutions were prepared as described in Section 5.2. The concentration of the platinum solutions used was about 0,006 M (approximately 1200 p.p.m.). Tin solutions were made up according to the desired Pt(II)/Sn(II) ratio so as to allow equal volumes of each metal solution to be used in an extraction. The concentration of the tin(II) was checked regularly by titration with KIO_3. Triphenylphosphine solutions of appropriate Pt/PPh_3 ratio were prepared so as to obtain equal volumes of organic and aqueous phases in the extractions.

The metal solutions, usually about 4 ml of each, were dispensed into a separating flask, fitted with a Teflon tap and previously flushed with nitrogen. The flasks were tightly stoppered using a small amount of grease and secured with parafilm plastic and two strong rubber bands. The aqueous phase was equilibrated by shaking on an automatic shaker for 20 minutes (1,5 M HCl solutions) or 10 minutes (1 M HCl solutions) as described in Section 3.1. A volume of TPP solution equal to that of the aqueous phase was added to the extraction vessel, taking care to exclude air during the process. The stopper was again secured tightly and the mixture was shaken for the desired time period. In each set of experiments, a blank was run using pure dichloromethane as the organic phase.

After extraction the organic phase was immediately run off and treated as desired. Portions of the aqueous phase were removed with a pipette for atomic absorption and uv-visible spectrophotometry.

5.9 Ultraviolet-Visible Spectrophotometry

Undiluted aqueous and organic phases were rapidly transferred, with a pasteur pipette, to quartz spectrophotometric cells, covered tightly with parafilm plastic to exclude air.

Due to the intensity of the red aqueous layers, 1 mm cells were used for all measurements. Two mm and 10 mm cells were used for the organic phases, depending on the colour intensity of the solutions.

A Superscan 3 Varian Ultraviolet-visible Spectrophotometer was used. 1 M or 1,5 M HCl and CH_2Cl_2 were used as blanks for the aqueous and organic phases respectively. Spectra were run between 200 and 600 nm using a slit width of 1,5 nm and scan speed of 100 nm/min.

5.10 Studies with Prepared Platinum-Tin Complexes

The complex [$PtCl_2(PPh_3)_2$] was prepared by the method of Jensen [89]. K_2PtCl_4 (1 g) in H_2O (20 ml) was mixed with PPh_3 (1,3 g) in hot ethanol (20 ml) and shaken for 24 hours. The white precipitate of *cis*-$PtCl_2(PPh_3)_2$ was filtered off and washed with water/ethanol and ether giving a yield of 95 %. The solid was dried under vacuum for 3 hours. (Found: C, 54.3; H, 3.9 %. Calc.: C, 54.69; H, 3.83 %).

The isomers *cis*- and *trans*-[$PtCl(SnCl_3)(PPh_3)_2$] were prepared according to Baird [45]. The *cis*-isomer was made by adding a concentrated solution of excess anhydrous $SnCl_2$ in acetone to a stirred suspension of *cis*-$PtCl_2(PPh_3)_2$ (0,5 g) in dry ether (25 ml). The experiment was carried out under nitrogen and an orange precipitate rapidly formed. The product was filtered, washed with ether and vacuum dried for 3 hours. Yield: 93 %. (Found: C, 44.8; H, 3.15 %. Calc.: C, 44.11; H, 3.09 %).

The *trans*-isomer was made by shaking *cis*-[$PtCl_2(PPh_3)_2$] in acetone with excess stannous chloride for 24 hours. Baird isolated the isomer after 10 - 15 minutes of stirring but we found that after this time the solution was still bright orange. Prolonged shaking resulted in the formation of a white/very pale yellow solid. The compound was filtered off and washed with acetone, giving a yield of 70 %. (Found: C, 44.2; H, 3.2 %. Calc.: C, 44.11; H, 3.09 %).

Experiments with the above compounds were carried out in the following way. Portions of the *cis*- and *trans*-isomers (0,01 g), finely ground, were dissolved in nitrogen-saturated CH_2Cl_2 (10 ml) in stoppered test-tubes. Hydrochloric acid (10 ml) of various concentrations was added to each test-tube and the samples were shaken for 3 hours. The aqueous layer was removed and analysed directly for tin content by atomic absorption to determine percentage back-extraction.

Cis-$[PtCl_2(PPh_3)_2]$ (0,06 g) was dissolved in nitrogen-saturated CH_2Cl_2 (5 ml) in a stoppered test-tube and shaken with 0,0140 M $SnCl_2$ (5 ml) in 1 M HCl for 18 hours. The aqueous phase was removed for direct analysis by atomic absorption to determine the amount of tin extracted into the organic phase.

The infrared spectra of the prepared complexes were all run as Nujol mulls between polyethylene plates on a Digilab FTS 16B/D interferometer from 400 to 80 cm^{-1}.

5.11 Isolation of Complexes from the Organic Phase

After separation from the aqueous layer, the dichloromethane was evaporated from the organic phase by gentle warming of the solution. The infrared spectra of the residues were obtained as described in Section 5.10.

An attempt was made to isolate pure $[PtCl_2(PPh_3)_2]$ from the organic phase (Figure 3.14) [90]. The solvent was removed from the organic layer leaving a mixture of yellow and white precipitate. The residue was extracted with benzene to give a yellow solution and a white precipitate which was filtered off. The latter was confirmed to be pure $PtCl_2(PPh_3)_2$ by infrared and micro-analytical data. (Found: C, 54.1; H, 3.8 %. Calc.: C, 54.69; H, 3.8 %).

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