THE SOLVENT EXTRACTION AND SEPARATION OF THE TETRACHLOROPLATINATE(II) AND -PALLADATE(II) IONS IN THE PRESENCE OF STANNOUS CHLORIDE INTO METHYLISOBUTYLKETONE

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ABSTRACT

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The potentialities of extracting platinum(II) and palladium(II) selectively as complexes of $[M(SnCl_3)_nCl_{4-n}]^{2-}$ (M=Pt,Pd) was examined. A study was made of the effect of $SnCl_2$ on the solvent extraction of K_2PtCl_4 and K_2PdCl_4 from solutions containing various concentrations of HCL into methylisobutylketone (MIBK)/hexane mixtures. It was found that increasing $SnCl_2$ concentrations dramatically increases the efficiency of extraction of platinum into the organic phase. In the presence of a five molar excess of $SnCl_2$, platinum is quantitatively extracted. In contrast, palladium is not quantitatively extracted under similar conditions. Our studies show that the percentage extraction of platinum and palladium depends upon the Sn(II):M(II) ratio, the HCL, H^+ and Cl^- concentrations and the equilibration time as well.

Studies were also carried out to investigate the possibility of separating platinum and palladium by varying the amount of $SnCl_2$ present. Results obtained showed that the separation was dependant on the HCL concentration of the aqueous phase and the composition of the organic phase. The effects of macroamounts of palladium and excess tin on the separation process was also examined. A preliminary study of the effect of four base metals on the separation was undertaken.

CHAPTER 1

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1. INTRODUCTION

Transport of materials from one phase to another is one of the most fundamental procedures for the separation of a chemical species from the medium or from other coexisting components. Thus distillation and condensation (liquid phase to gas phase and vice versa), dissolution and crystallisation or precipitation (solid phase to liquid phase and vice versa), and sublimation (solid phase to gas phase and vice versa) have been employed in various experiments since the early days of chemistry [1].

Recent advances in analytical chemistry are characterised by great progress towards more powerful methods of separation. One of these methods, namely solvent extraction, is also a type of interphase transport process; and from this point of view, it should be regarded as essentially the same kind of experimental technique as the above-mentioned classical methods. Because of its ease, simplicity, speed and wide scope, solvent extraction enjoys a favoured position among the separation techniques and is becoming more and more important in inorganic and analytical chemistry.

It permits simpler and cleaner separation of materials at both macro and tracer level concentrations, utilising apparatus no more complicated than a separatory funnel and requiring several minutes at most to perform, yet contamination from other components is less than that found in other existing methods [2, 3, 4].

1.1 Theory of Solvent Extraction

Solvent (or liquid-liquid) extraction is defined as the partition of one or more solutes between two immiscible or partly miscible liquid phases [5]. If two immiscible liquids are placed in contact with any substance soluble in both of them, this substance will distribute or partition itself between the two phases in a definite proportion depending on its respective solubilities and on the relative volumes of the two solvents.

In certain cases, a substance dissolved in one phase, for example, in an aqueous solution, can be completely transferred to the second phase, which is often an organic liquid. This is the basic principle of liquid-liquid extraction which is employed in so many analytical separations and which forms the basis of an increasing number of commercial and large-scale industrial processes.

Because most inorganic species are only very slightly soluble in the majority of inert, water-immiscible organic solvents, their extraction can only be brought about through interaction with an organic molecule which produces a less hydrophilic species. This active material is termed the extracting agent. The organic phase may either be a pure extracting agent alone (eg methyl isobutylketone or tributyl phosphate) or a solution of the extracting agent in a suitable water-immiscible diluent (such as kerosene, carbon tetrachloride or hexane). Sometimes, especially in industrial applications, an additional component, the modifier, is included to confer some beneficial properties to the extraction system such as ease and speed of phase separation. In summary, then, the effective extracting ("organic") phase comprises the active extracting agent together with any diluent and modifier. In analytical practice, the term extractant is often used for the extracting agent only.

1.1.1 *The Phase Rule*

A useful rule summarising the general properties of liquid-liquid distribution systems, is the phase rule which is usually given as

$$P + F = C + 2 \qquad [1]$$

where P, F and C denote the number of phases, degrees of freedom and components respectively. In the simplest case of two components forming 3 phases (two liquid and one vapour), it follows that the number of degrees of freedom F is 1. If the temperature is fixed, then both the vapour pressure and the compositions of the two phases are fixed. The percentage composition of each phase is independent of the total amount of each component, and the volumes of the phases can be altered at will.

When a system contains only one solute (C=3), the degree of freedom is 2. At fixed temperature and pressure the concentration of one component (usually termed the solute) in one of the liquid phases is fixed; it follows that the concentration of that component in the second immiscible phase must be fixed also. Thus when the 'molecular weight' of the solute is the same in the two phases, the concentration is proportional to that in the other phase. Hence, we see that there will therefore be a definite relationship between the solute concentrations distributed between the two phases, which is the basis of the distribution law.

1.1.2 *The Distribution Law*

The distribution law, first presented in 1872 by Berthelot and Jungfleisch [6] and systemised thermodynamically in 1891 by Nernst [7] is the most fundamental rule in solvent extraction chemistry [1]. Thus a solute will distribute between two immiscible solvents in such a manner that, at equilibrium, the ratio of the concentrations of the solute in the two phases at a particular temperature will be a constant, provided the solute has the same molecular weight in each phase. For a solute partitioning between two immiscible phases distinguished by the subscripts 1 and 2, we have

$$X_1 \rightleftharpoons X_2$$

$$\frac{[X]_2}{[X]_1} = (K_d)_X \qquad (2)$$

where $[X]_1$ is the concentration of the species X in phase i and K_d is the distribution or partition coefficient, a constant that has experimentally been found to be independent of the total concentration of solute in the whole system and also of the actual phase volumes.

1.1.3 *The Distribution Ratio*

Chemical interactions of the distributing species with the other components in each phase are of great significance since these interactions can profoundly affect the concentration of the distributing species. Since we are more concerned in the overall or stoichiometric distribution of the component of interest between the phases in a solvent extraction system, it becomes necessary to introduce a more practical quantity to describe the extraction, the distribution ratio, D, which is usually expressed by the ratio of the concentration in the two phases.

$$D = \frac{\text{Total concentration in organic phase}}{\text{Total concentration in aqueous phase}} \qquad (3)$$

This is a stoichiometric ratio including all species of the same component in the respective phases. The fact that the distribution ratio is a dimensionless quantity is an important characteristic of solvent extraction equilibrium.

1.1.4 *Percentage Extraction*

Although the use of the distribution ratio is advantageous for a fundamental study of the distribution equilibria, the extraction is very often expressed for convenience as the percentage extraction, %E. The relationship between the distribution ratio and the percentage extraction is given by the following equation:

$$\%E = \frac{D \times 100}{D + (V_{aq}/V_{org})} \qquad (4)$$

where V_{aq} and V_{org} represent the volumes of the aqueous and organic phases respectively. When the volumes are equal, the denominator simplifies to D + 1 therefore

$$\%E = \frac{D \times 100}{D + 1} \qquad (5)$$

Substituting equation (3) into equation (5) yields

$$\%E = \frac{100.\ \text{Total concentration in organic}}{\text{Total concentration in organic} + \text{Total concentration in aqueous}}$$

$$= \frac{100.C_{org}}{C_{org} + C_{aq}}$$

which can be expressed as

$$\%E = \frac{C_{total} - C_{aqueous}}{C_{tot}} \times 100 \qquad (6)$$

1.1.5 *Formation of Extractable Metal Complexes*

Ionic compounds would not be expected to extract into organic solvents from aqueous solution because of the large loss in electrostatic solvation energy which would occur. The most obvious way to make an aqueous ionic species extractable is to neutralise its charge which would involve reactions of the metal in the aqueous phase leading to the formation of a neutral extractable species. This can be accomplished by co-ordination, either simple monodentate co-ordination or chelation, or by ion association; the larger and more hydrophobic the resulting molecular species the better will be its extraction.

The case of co-ordination may be described by

$$M^{n+} + nR^- \rightleftharpoons MR_n \qquad (7)$$

where M^{n+} is an n-valent metal ion and R^- is an anionic ligand.

Amongst the many kinds of co-ordination complexes, two types may be distinguished. First there are the simple co-ordination complexes in which metal ions combine with monofunctional ligands in a number equal to their co-ordination number. Germanium tetrachloride ($GeCl_4$) is an example of this type of extractable species involving co-ordination.

A second category includes the interaction of metal ions with polyfunctional ligands. These are called chelate complexes. The functional groups of the ligand must be so situated in the molecule that they permit the formation of a stable ring, generally five or six-membered eg. copper(II) 'acetylacetonate'.

In addition to co-ordination compounds, there are a large number of uncharged components formed by the association of oppositely charged ions in pairs or clusters of higher order. A major fraction of the extractable species other than those that are chelates exist in the organic solvent as ion-association aggregates, as summarised below:

$$A^+ + B^- \rightleftarrows (A^+, B^-) \qquad (8)$$

The following types of ion-association complexes may be recognised:

(i) those formed from a reagent yielding a large organic ion which forms large ion aggregates or clusters with suitable oppositely charged ions

(ii) those involving a cationic or anionic chelate complex of a metal ion and

(iii) those in which solvent molecules are directly involved in formation of the ion-association complex.

1.2 The Platinum - Tin Complex

It has long been known that the interaction of tin(II) chloride with solutions of platinum and other platinum-metal salts in aqueous or alcoholic solution gives coloured species [8], whose composition has, in recent years, been the subject of much study. The characteristic intense-red coloured complexes produced when solutions of $SnCl_2$ and $PtCl_4^{2-}/PtCl_6^{2-}$ are mixed was first discovered and reported by Wöhler [8] and has subsequently been used for determining small amounts of platinum [9-11].

The complexes formed between platinum and tin(II) chloride are, in addition, of considerable interest because of their high catalytic activity towards hydrogenation and isomerisation reactions. Many authors have accordingly tried to isolate the complexes which are formed and to study their properties; however, there is still lack of agreement regarding the nature and compositions of these complexes and the formal oxidation state of platinum in them [12-14].

Wöhler and Spengel [15] suggested that the colour produced in the reaction of platinum(IV) and tin(II) chloride was due to colloidal platinum but reported no definite stoichiometry. Ayres and Meyer [16] disproved this postulate by observing that the coloured material readily passes through semipermeable membranes such as colloidion. Further evidence that the coloured species is not the colloidal metal is shown by the extractability of the red colour into organic solvents. Later authors have attributed the colour to platinum(II) [17], or to chloroplatinous acid [18, 19].

Most workers have assigned to platinum an oxidation state of two and co-ordination numbers of 2 to 5 with respect to the $SnCl_3^-$ ligand. However, in contrast to this overwhelming body of evidence, Ayres and Meyer [12] and also Lindsey and co-workers [14] have detected tin(IV) in the solutions and suggested that the platinum has zero valency. In another study of the oxidation state of platinum in its compounds with tin(II) chloride by polarographic and potentiometric methods, it was established that complex formation with tin(II) involves not bivalent platinum but zero valent platinum [20].

Extensive spectrophotometric studies by Ayres and Meyer [12] on the reaction between Pt(II) and tin(II) chloride established 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 principle product corresponding to a tin to platinum ratio of 5:1. Spectrophotometric methods and precipitation tests indicated the presence of a tetrapositive cationic complex containing platinum (0), tin(II) and chloride, to which the formula $[PtSn_4Cl_4]^{4+}$ was tentatively assigned.

Young *et al* [13] determined the structure of a number of platinum-metal-tin complexes showing that they were anionic with the following structures: $[PtCl_2(SnCl_3)_2]^{2-}$, $[RuCl_2(SnCl_3)_2]^{2-}$, $[Rh_2Cl_2(SnCl_3)_4]^{4-}$ and $[Ir_2Cl_6(SnCl_3)_4]^{4-}$. Electrophoretic studies by Shukla [21] also demonstrated the presence of anionic species in both the platinum-tin and rhodium-tin systems in dilute hydrochloric acid solution, an observation confirmed by an ion-exchange study carried out by Davies *et al* [22]. The ruthenium-tin complex was also shown to be anionic and to be precipitated by large cations [23]. Cramer and co-workers [24] have established the existence of complex anions for the platinum-tin system and have also isolated neutral complexes as their triphenylphosphine derivatives. The extractability of the platinum-tin complex by high molecular weight amines in organic solvents [25] further suggests that the coloured species is anionic in nature, in agreement with the suggestions of Shukla [21] and findings of Young *et al*.

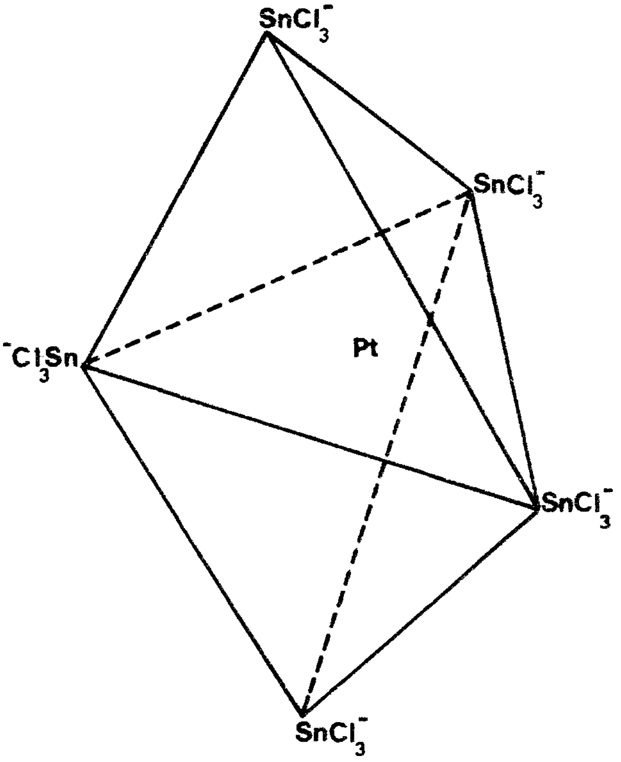
Elizarova and Matvienko [26] state that data obtained during spectrophotometric studies by Ayres and Meyer [12] and Davies *et al* [22] are contradictory because their investigations were carried out over a narrow concentration range of extractants. In their detailed spectrophotometric study they show that platinum reacts with tin(II) chloride in solutions with a chloride concentration of 1-2M and a constant ionic strength of $\mu = 2$ to form two complexes with Pt:Sn ratios of 1:1 and 1:2. They also suggest that the 1:2 platinum complexes with tin(II) chloride can exist in *cis* and *trans* -forms.

Young and his co-workers [13] have been able to isolate the proposed square-planar *cis* and *trans* -isomers of $[PtCl_2(SnCl_3)_2]^{2-}$ as the tetramethylammonium salts, one of which is red and the other yellow. Although it has not been possible to determine unequivocally the configurations of the two isomers, Young *et al* [13] considered the yellow form to be the *cis* - isomer. Some $d_\pi - d_\pi$ bonding between platinum and tin is expected which would cause the *cis* -isomer to be more stable than the *trans* - because in the latter configuration there will be competition between the two $SnCl_3^-$ groups for the same d-orbitals of platinum and hence weaker π-bonding. Thus, while the red form is favoured kinetically, the yellow is probably more stable thermodynamically.

The *cis* - and *trans* -ion are both thought to exist in solutions of low Sn:Pt ratios, with the concentration of the red form increasing with increasing Sn:Pt ratio. Solutions containing Sn:Pt ratios greater than 2:1 yielded red salts which frequently contained more than 2 moles of tin per mole of platinum, up to a limiting ratio of 5:1.

It was thus proposed that high Sn:Pt ratios led to the existence of red complexes in solution in which tin was co-ordinated to platinum to give a predominantly quinqueco-ordinated ion, $[Pt(SnCl_3)_5]^{3-}$. Determination of the configuration of the $[Pt(SnCl_3)_5]^{3-}$ anion by X-ray diffraction [27] has shown it to be a trigonal bipyramid consisting of a central platinum atom in the equatorial plane surrounded by five $SnCl_3^-$ ligands at the apices attached through Pt-Sn bonds. Because the $SnCl_3^-$ ligand is a weak σ-donor and a strong π-acceptor [28], 5 $SnCl_3^-$ ligands may be co-ordinated about platinum without excessive build-up of electron density on the central metal atom as has now been established for $[Pt(SnCl_3)_5]^{3-}$.

Mössbauer spectroscopic studies of trichlorostannyl platinum(II) complexes have shown that the red complexes namely the *trans* - $[PtCl_2(SnCl_3)_2]^{2-}$ and $[Pt(SnCl_3)_5]^{3-}$ anions have identical Mössbauer and infrared parameters [29]. It was therefore probable that a mixture of Pt-Sn complexes are the species giving the red colours to solutions of platinum and tin.



In conclusion therefore it may be said that the red species formed in solution appears to be

(i) due to one of $[PtCl_{4-n}(SnCl_3)_n]^{2-}$ (n=1 to 4) and $[Pt(SnCl_3)_5]^{3-}$ or a mixture of these

(ii) anionic in nature containing both platinum and tin in the divalent oxidation state.

1.3 The Palladium - Tin Complex

Stannous chloride reacts with palladium chloride in hydrochloric acid solution, giving a series of colour changes that vary with the concentration of the acid [30]. The orange-red colour produced when palladium(II) chloride solutions treated with tin(II) and mercury(II) chlorides in hydrochloric acid was reported by Pollard [31] as a specific qualitative spot test for palladium.

Ayres and Meyer [16] observed that an intense red-orange colour developed with the first few drops of tin(II) chloride; further addition of the reagent eventually resulted in a dark olive-green solution. The coloured compound formed with stannous chloride was found to be extractable into organic solvents such as ethylether, ethylacetate, amylacetate and octylalcohol [32].

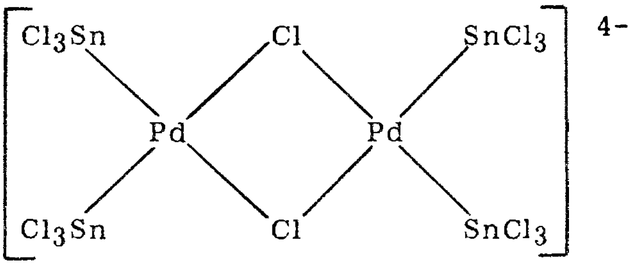
Further studies showed that the amount of palladium extracted depended both upon the concentration of hydrochloric acid and the concentration of tin(II) chloride. Lower hydrochloric acid concentrations were found to increase the extractability of the colour into the organic phase, whereas increased concentrations of tin(II) chloride finally resulted in the formation of an olive-green material which was extractable only to a slight extent. It was proposed that this material was probably the metal in the colloidal state [16].

The complexes of Pd(II) with tin(II) halides have been least studied. Young *et al* [13] studied the structure of the chlorotin complexes of the platinum-group metals but omitted the palladium complex probably due to the unstable complex that is formed.

Khattak and Magee [33] began investigations on the Pd(II) - Sn(II) system by determining the structure of the complex formed. Attempts by them to precipitate the palladium-tin anionic chloro-complex using tetraphenylarsonium chloride were successful, but only after numerous trial experiments were performed to establish the most favourable conditions. On the basis of their analytical data they suggested the following formula for the precipitated compound:

$$[(C_6H_5)_4As]_2\ [PdCl(SnCl_3)_2]$$

It was proposed that the structural formula for the palladium-tin anionic chloro-complex may be written as:



Further investigations by these authors involved determination of the extractability of the complexes formed between Pd(II) and Sn(II) in hydrochloric acid by tri-n-octylamine [34]. Two different complexes were obtained : one a brown-red complex and the other a yellow coloured complex. Both were easily extracted into tri-n-octylamine in benzene but the fact that 2 different complexes existed indicated the instability of the system in the aqueous phase. In contrast to the absorption spectrum of the red-brown species, the yellow species possessed a definite absorption maximum at 410 nm in the amine phase indicating that the complex in the aqueous phase is stabilised by extraction into the amine.

From the ease with which complexes formed between Pd(II) and tin(II) are extracted into tri-n-octylamine, it was assumed that the species were anionic and that 'ligand anion exchange' occurs between the complex and amine. Confirmation of this is given by previous work [33] and it was therefore proposed that the extraction of the anionic species may be represented by an overall reaction of the type:

(i) $R_3N + H^+A^-_{aq} \rightleftarrows R_3NH^+A^-_{org}$

(ii) $PdCl_2 + 2SnCl_2 \rightleftarrows [PdCl(SnCl_3)_2]^{2-}$

(iii) $2R_3NH^+A^- + [PdCl(SnCl_3)_2]^{2-}_{aq} \rightleftarrows [R_3NH^+]_2\ PdCl(SnCl_3)_2 + 2A^-$

where H^+A_{aq} represents hydrochloric acid and R_3N represents tri-n-octylamine.

A systematic study of the conditions of formation of the complexes of Pd(II) with tin(II) chloride in solution showed the existence of at least 3 complex species, depending on the concentration conditions [35]. In addition to the red and yellow complexes postulated to be formed by Khattak and Magee [34], a third more stable green form of complex was also found to exist. The overall light absorption spectra of solutions containing Pd (II) and different quantities of tin(II) chloride revealed that a yellow complex species (λ max = 420 nm) is formed which is slowly converted into a green form (λ max = 635 nm) depending on the tin(II) chloride concentration.

Sufficiently high concentrations of tin(II) chloride led to the rapid formation of the yellow and a new red form which were rapidly converted into a stable green form. With further increase in tin(II) chloride concentration, the colour of the solution turned from green to brown. It was suggested that this brown solution is a colloidal solution from which metallic palladium gradually separated.

Both the yellow and red complexes could be extracted into polar solvents indicating that they were charged complexes. The red complex of palladium with tin(II) chloride appeared to be a shortlived species, unstable towards atmospheric oxygen and converted into the yellow form in 5-10 minutes. Absorption spectra of the red form in 3-methylbutanol revealed 2 absorption bands: one at λ = 355 nm characteristic of the red form and the other at 420-430 nm which is characteristic of the yellow form. This indicated that the red and yellow forms were present in a state of dynamic equilibrium.

The most stable complex of palladium(II) with tin(II) in aqueous solutions is the green form which is produced at all tin(II) chloride concentrations (λmax = 635, 465 and 380 nm). Kinetic studies of the formation of the green complex at 635 nm revealed that the green form is produced slowly at low tin(II) chloride concentrations, but increase in tin(II) chloride concentrations led to rapid production of the green form.

Zayats *et al* [36] found that the nature of interaction in the $PdCl_2$-$SnCl_2$-HCL-H_20 system depends on the molar ratio of $PdCl_2$ and $SnCl_2$ in solution as well as on the total concentrations of metal salts and acid. In solutions with a $PdCl_2$:$SnCl_2$ molar ratio of 1:2 or less, an unstable palladium hydrosol is formed as a result of the reaction:

$$Pd^{2+} + Sn^{2+} \rightleftarrows Pd^o + Sn^{4+}$$

Absence of characteristic bands on the absorption spectra indicated that no complexes are formed at this molar ratio.

At constant ratios of $PdCl_2$ and $SnCl_2$ concentrations the composition and stability of complexes formed was found to depend on the concentrations of acid. For example, in the formation of complexes at $PdCl_2$:$SnCl_2$ = 1:8 in 0.5M HCL in a freshly prepared solution the green complex was mainly formed, in 2M the yellow and in 8M the stable red-brown form. Such a relationship was also obtained at a ratio of concentrations in the solution of $PdCl_2$:$SnCl_2$ = 1:40.

The complex formation of test solutions was also found to depend on the total concentration of the metal salts. It was found that at fixed $PdCl_2$:$SnCl_2$ ratios, a considerable decrease in the total concentration of metal salts in the solution irrespective of the acidity resulted in the formation of yellow complexes. Proof of this lies in the fact that at 2M HCL the interaction of components led to the formation of mainly the green complex in more concentrated metal salt solutions while the yellow form predominated in dilute solutions. However in 8M HCL an unstable blue-violet complex is formed in concentrated solutions which is converted into a stable red-brown form; but the yellow form appeared in dilute solutions.

In summary, it appears that as in the case of platinum, the palladium-tin complex is anionic and extractable into organic solvents. In contrast to platinum however, a number of species of the palladium-tin complex are postulated to exist depending on the conditions in solution. The green palladium-tin complex appears to predominate over the other forms. However, no attempt has been made to determine the structure(s) of these different complexes presumably due to the instability of the palladium-tin system in the aqueous phase.

1.4 Solvent Extraction and Separation of Platinum and Palladium

Solvent extraction is widely used for the isolation and separation of the noble metals [37, 38]. It is probably the most efficient method for the separation of the platinum elements whose chemical properties are so strikingly similar, and its high selectivity and use of relatively cheap reagents can make it an economically viable proposition for the extraction of the precious metals.

The analysis of the platinum-group metals is complicated by the fact that very rarely does only one of them occur in the material to be analysed. In most cases, the platinum-bearing materials submitted for analysis also contain palladium, rhodium, iridium, ruthenium and osmium as constituents. In some instances, the amount of platinum and palladium relative to the other members of the group is extremely high and serious problems arise when such samples are to be analysed for all the noble metals [39].

Atomic absorption spectroscopy (AAS) is complicated for the direct measurement of platinum, palladium, rhodium and iridium in noble metal mixtures because of mutual interferences. Their determination is also affected by interferences from base metals. Usually, before the determination of each metal, a separation is imperative and the separation step definitely represents the most difficult problem of the analysis, especially in the case of micro amounts. Such problems may be overcome using a solvent extraction technique which is selective, fast and simple to use.

The platinum metals can exist in several oxidation states and these states tend to be easily interchangeable with each other in aqueous solution in the presence of extractants which act as reductants or oxidants of the metal ions [40]. Hence the solvent extraction behaviour of the platinum metals is quite complicated, as are their other chemical properties in solutions.

Another remarkable characteristic of platinum metals which affects their solvent extraction behaviour is that the rate of complex formation of their metal ions is sometimes extremely slow. These metals are extractable in some systems only when they are treated with extractant on boiling or when the metal ions and the extractants are in contact for some time. For these reasons, experimental data on the solvent extraction of the platinum metals are sometimes not reproducible and the chemical form of the extracted metal species in the organic phase is not always very clear [40].

The extraction of platinum metals from HCL with MIBK [41], TBP [42, 43], TOPO [41] and various organophosphorous compounds [44] have been studied. In many systems platinum is coextracted with palladium(II), and, although the extraction behaviour of these two metal ions is somewhat different from each other, their mutual separation is usually not very easy.

Great potential lies in the use of amine extraction systems for the solvent extraction of the precious metals. These systems exploit the strong tendency of precious metals to form anionic complexes in solution which easily distinguishes them from base metal contaminants. High molecular weight amines (HMWA) were first used as extractants by Smith and Page [45]. Khattak and Magee [25] investigated the application of HMWA for the extraction of platinum in the presence of associated base and noble metals. The amines recommended were tri-n-hexylamine, tri-n-octylamine and primene dissolved in chloroform or benzene. Separation from palladium involved careful addition of ammonia, then concentrated hydrochloric acid and tin(II) chloride solution without delay, extraction, filtration and dilution to volume with pure solvent.

Triphenylphosphine and other phosphines (arsines and stibenes) form complexes of the type $MeCl_nL_m$ with the platinum metals [46]. Solvent extraction studies of compounds of platinum metal halides with these phosphines have been made [47, 48]. The possibility of extracting palladium with triphenylphosphine was first pointed out by Senise and Levi [48]. Ruthenium, silver and gold were also found to be extractable from acidic aqueous solutions into triphenylphosphine in an organic solvent such as benzene or toluene [47, 49]. In view of this, Mojski [46] examined the extraction of the platinum metals from hydrochloric acid medium with triphenylphosphine (TPP) in 1,2- dichloroethane and found that the presence of a large excess of stannous chloride resulted in marked differences in the extractability of the platinum group metals. Detailed studies by Yates [50] on the solvent extractability of platinum(II) by TPP in dichloromethane revealed that $SnCl_2$ dramatically increased the rate and efficiency of extraction.

The solvent extraction of platinum metals in the presence of tin(II) chloride has been investigated by many Russian and independent workers. Many solvents such as di-o-tolylthiourea [51], diphenylthiourea [52] and dimethylsulfoxide [53] have been used as suitable extractants for the platinum group metals.

The separation of platinum from palladium can present difficulties because of similar chemical properties. However, the use of a variety of reagents have made available many effective methods of extractive separation of platinum and palladium. Egli [54] used 2-chloropyridine to separate and determine palladium and platinum. Thioxine (8-quinolinethiol) was used by Lystova and Strel'nikova to separate palladium and platinum with palladium determined in the organic phase and platinum in the aqueous acid phase. Thiourea was added to mask the platinum, and the palladium complex was formed with thioxine which was subsequently extracted with chloroform.

Various methods of determining platinum and palladium in rocks etc. have been described. Grimaldi and Schnepfe [55] used conventional methods of separation and determination. The sample was dissolved in appropriate acids and tellurium was added to precipitate both platinum and palladium. The latter metals were extracted from the mixed precipitate by MIBK. Palladium was determined by selective extraction as the α-furildioxime in chloroform and the aqueous phase was used to determine platinum by the colorimetric tin(II) chloride method.

A solvent extraction separation of platinum and palladium from rhodium and iridium was described by Kashlinskaya *et al* [56]. The solution of the four metals as complex chlorides was treated to form the iodides. The complex iodides of platinum and palladium were extracted by butyl phosphate. This organic phase was extracted with nitric acid to extract platinum and palladium which were then determined photometrically.

Faye and Inman [57] described a procedure in which the platinum and palladium iodides were isolated simultaneously and selectively removed from rhodium and iridium by two extractions with tributyl phosphate (TBP) in hexane followed by three aqueous extractions with nitric acid. For the separation of palladium, aliquots of the nitric acid extract were used and platinum and palladium were separated and determined with p-nitrosodimethylaniline by a procedure based largely on the early work of Yoe and Kirkland [58].

1.5 Objectives of Research

In September 1974 Gorbanev *et al* [59] read a paper at the International Solvent Extraction Conference in Lyon dealing with the extraction of 'cluster' complexes between the noble metals and tin(II) chloride into a number of oxygen-containing solvents. The investigation dealing largely with spectroscopic (Mössbauer) details and attempting to discuss all the platinum-group metals at once, was not reported in detail. Literature data concerning further work in this regard was found to be lacking and it was thus decided to examine in greater detail the effect of $SnCl_2$ on the solvent extraction and separation of platinum(II) and palladium(II).

The objectives of this work may now be summarised as follows:

(a) To investigate the effect of stannous chloride on the extraction of platinum(II) from aqueous hydrochloric acid solutions of $K_2P_tCl_4$ into hexane containing methylisobutylketone (MIBK).

(b) To examine the effect of

- (i) the Sn(II):Pt(II) molar ratio
- (ii) hydrochloric acid concentration
- (iii) chloride concentration
- (iv) hydrogen ion concentration
- (v) equilibration time

on the extraction of platinum in the form of the trichlorostannatoplatinum(II) chloride complex(es).

(c) To investigate the extraction of palladium by similar means as for platinum with the aim of possibly separating platinum and palladium using stannous chloride.

(d) To investigate the optimum conditions for extraction or separation of platinum and palladium.

(e) To make a preliminary study of the effect of a variety of base metals (most likely to be associated with the platinum group metals) on the separation process.

CHAPTER 2

CHAPTER 2

2. PRELIMINARY INVESTIGATIONS

2.1 Methods of Analysis

Atomic absorption spectroscopy (AAS), a widely used technique for the analysis of over sixty elements, has been a popular analytical method for determining the noble metals, and has permitted the analysis of many different noble metal samples [60]. 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 has thus been considered suitable for the determination of the noble metals and was used for the analysis of platinum/ palladium and tin in the presence of each other in the aqueous acid medium.

2.1.1 *Atomic Absorption Determination of Platinum*

The determination of platinum by atomic absorption spectroscopy has been reported in a number of papers [61]. Recently new procedures were recommended for the determination of platinum in aqueous solutions by AAS using both air-acetylene and nitrous oxide-acetylene flames [60, 62]. However, air-acetylene mixtures are generally favoured, with very lean clear, blue strongly oxidising flames providing maximum sensitivity for platinum. The most obvious reason for avoiding high-temperature flames such as nitrous oxide-acetylene has been the reduction of platinum sensitivity owing to ionisation interferences. The platinum resonance line at 265.9 nm was used for all measurements in this work since it is the most sensitive and has the lowest background noise.

The use of organic solvents has had an important impact on the atomic absorption method. Large increases in analytical sensitivity of many elements has been obtained either by addition of miscible solvents to aqueous solutions or by the solvent extraction of the elements into an immiscible solvent layer before their determination [63 - 65].

Although platinum sensitivity may be increased by using miscible solvents, in some cases the increased sensitivity is counterbalanced by the extra dilution imposed by adding the organic solvent. Clearly, a suitable solvent extraction system in which platinum is completely extracted into an immiscible solvent layer would have several further advantages. The determination of platinum in the organic phase would enhance the sensitivity by a factor of 3 or more and secondly, platinum in large aqueous volumes could be concentrated into a small volume of the organic phase thus increasing the detection limit.

The most widely used immiscible extracting solvent in AAS is 4 methyl-2-pentanone (MIBK) [66]. Mulford [67] described a general solvent extraction system in which a non-specific reagent, ammonium pyrrolidine-dithiocarbamate (APDC), was used to form chelates with many metals including platinum, followed by solvent extraction into MIBK. However MIBK's partial solubility in the aqueous phase can be a problem when extracting standards and samples at different organic-to-aqueous ratios. At any given organic solvent volume the loss of MIBK to the aqueous phase will be proportionately higher and therefore its solubility in the aqueous phase is thus an important consideration to take into account in an analysis [66]. Furthermore, since organic solvents act as a fuel when aspirated into the burner, the acetylene fuel flow has to be adjusted and strictly monitored in order to compensate for the organic solvent present in solution and to maintain reproducible flame conditions. Hence, because of the problems associated with direct analysis of our organic phases we decided instead to do atomic absorption determinations on the aqueous phases.

In the determination of platinum in aqueous acid solutions by AAS, serious depressive interelement interferences are encountered, particularly from the noble metals themselves (mutual interferences) and also from other metals and non-metals. To overcome the depressive interferences from various metals, Strasheim and Wessels [68] recommended that platinum be determined in the presence of sufficient copper sulphate ($CuSO_4$) to maintain the copper concentration at 2%. Although effective, the high salt concentration led to some problems such as burner clogging.

In her investigations Yates [50] found that the use of 2% $CuSO_4$ would successfully suppress interferences in determining platinum by AAS. In addition however, she showed that the addition of stannous chloride at high acidities seriously affected the absorbance readings that she had obtained and she attributed this to the reduction of copper(II) by tin(II).

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

The use of $CuSO_4$ was thus not suitable as an interference supressant for platinum in this work.

To overcome the depressive interferences from various metals, we chose $La(NO_3)_3$ as an interference suppressant as recommended by Vasilyeva *et al* [69]. Yates [50] showed that 0.2% $La(NO_3)_3$ is suitable to suppress interferences in platinum solutions of 1.0 to 3.0 M HCL with tin : platinum molar ratios of up to 10.

We 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 the appropriate acid concentration to match the matrix of the samples as closely as possible. Beer's law was obeyed for 0-120 ppm of platinum under these conditions. A typical calibration curve obtained in this way is shown in Figure 2.1

2.1.2 *Atomic Absorption Determination of Palladium*

Atomic Absorption Spectroscopy of palladium was first described by Lockyer and Hames [70] who used a low-temperature flame and reported a sensitivity of 1 ppm at the 247.68 nm line. Since

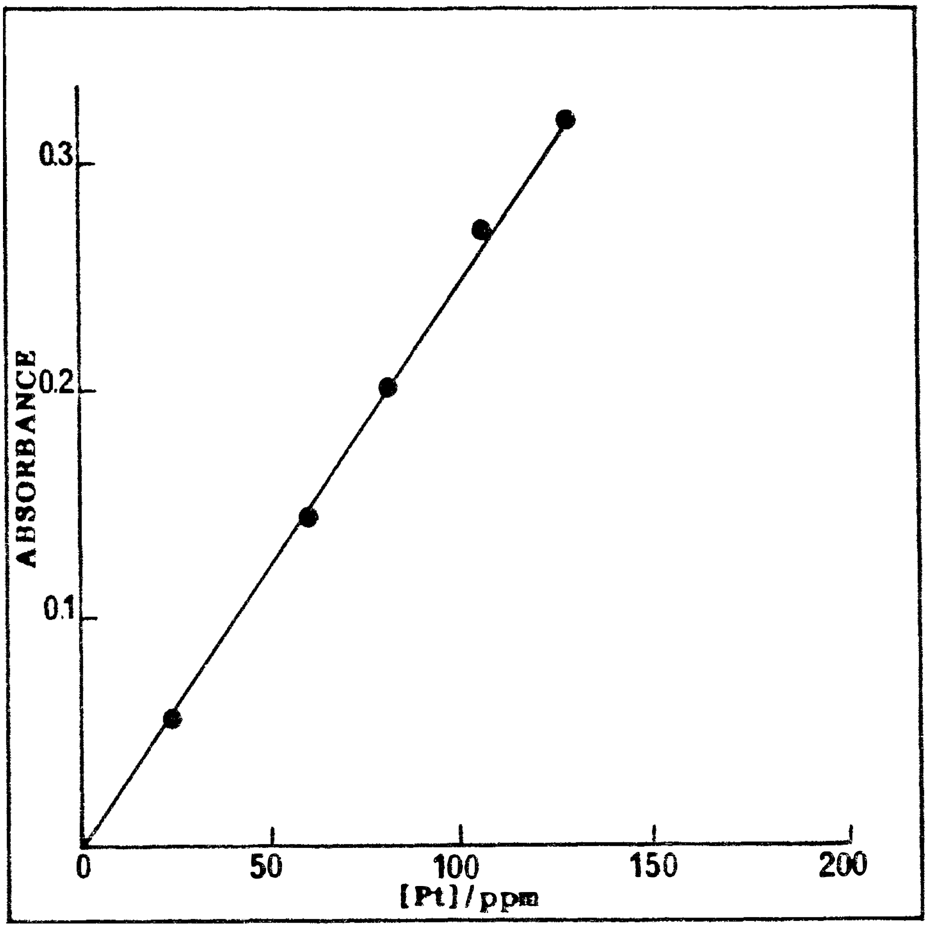


Figure 2.1 A calibration curve for platinum in 1.4M HCL with 0.2% $La(NO_3)_3$ and stannous chloride (Sn:Pt ratio = 10)

then several other authors have reported palladium absorption at various analytical lines and in various flames [71].

The determination of palladium by AAS is accompanied by few, if any, interferences [72]. Most authors have found no interference from a number of elements (including noble metals) and various acids. In contrast to some reports [66,67,70], several significant chemical interferences were observed in the determination of palladium in a cool air-hydrogen flame e.g. from Ni, Co, Fe etc., even when the concentration of acids in the investigated solutions were matched. It is also reported that the determination of palladium, even in the hotter air-acetylene flame, does not appear to be completely free of interferences; especially high concentrations of other noble metals can exert certain influences [73].

Sen Gupta [74] noticed interelement interferences in the determination of Rh, Pd, Ag, Ir, Pt and Au in a matrix in which one or more platinum-group metals were present in major quantities. The interference effects were mostly eliminated by buffering the solution with 0.5% Cu and 0.5% Cd (added as sulphate) or 1% La or 1% Sr. Schnepfe and Grimaldi [72], in the determination of palladium and platinum, also found that mutual and base-metal interferences were removed by the addition of a mixture of copper and cadmium sulphates.

Mallet *et al* [75] found lanthanum and uranium as the most effective releasing agents for the mutual interferences of all the noble metals whereas Pannetier and Toffoli [76] observed that the use of 0.5% Li, added as sulphate, in an air-acetylene flame not only enhanced the sensitivity of Pt, Rh and Ir but also eliminated interelement interferences in the determination of these 3 elements and palladium.

Strongly oxidising air-acetylene flames were used in the determination of palladium by AAS in this work. The 276.3 nm Pd line was used for all measurements.

The absorbance of palladium decreases with an increase in the concentration of hydrochloric acid. Results showing the effect on the absorbance value due to variations in acid concentration are shown in Table 2.1.

The absorbance for 50 ppm palladium in 5M hydrochloric acid is about 5% less than that for a solution containing 1M acid. The decrease in palladium absorbance is not considered to be a chemical effect but may be attributed to changes in physical properties of the solutions which affect the efficiency of transporta-

$[Pd^{2+}]$/ppm	[HCL]/M	Absorbance
50	1M	0.208
50	2M	0.207
50	3M	0.205
50	4M	0.199
50	5M	0.198

Table 2.1 The effect of hydrochloric acid on the absorbance of palladium

tion and atomisation of the analyte into the flame. These effects are a result of lower sample flow rates, changes in solution density and viscosity and different droplet sizes in the flame when working with concentrated solutions. In our work, we compensated for this affect by preparing matched matrix standards.

Because of conflicting reports in the literature as to whether the determination of palladium by AAS is accompanied by interferences or not, we decided to investigate whether interferences are in fact encountered and if any, attempt to eliminate these with the use of releasing agents viz. $La(NO_3)_3$, $LaCl_3$ and UO_2 as recommended by Van Loon [77] and Scarborough [78] amongst others.

From the results given in Tables 2.2, 2.3 and 2.4 it is evident that none of the three interference suppressants examined have an effect on the absorbance of palladium. This led us to believe that the determination of palladium in solutions containing no other metals by AAS is accompanied by no significant interferences.

Investigations were carried out to determine whether stannous chloride interferes in the determination of palladium by AAS in various acid concentrations. From the results shown in Table 2.5 it is evident that the stannous chloride has no effect on palladium solutions of 1-5M hydrochloric acid with tin : palladium ratios of up to 10.

[Pd^{2+}]/ppm	[HCL]/M	$La(NO_3)_3$/%	Absorbance
50	1M	0.5	0.208
50	2M	0.5	0.209
50	3M	0.5	0.207
50	4M	0.5	0.205
50	5M	0.5	0.200

Table 2.2 The effect of 0.5% $La(NO_3)_3$ on the absorbance of palladium

[Pd^{2+}]/ppm	[HCL]/M	$LaCl_3$/%	Absorbance
50	1M	0.5	0.208
50	2M	0.5	0.205
50	3M	0.5	0.203
50	4M	0.5	0.199
50	5M	0.5	0.200

Table 2.3 The effect of 0.5% $LaCl_3$ on the absorbance of palladium

[Pd^{2+}]/ppm	[HCL]/M	$U0_2$/%	Absorbance
50	1M	0.5	0.208
50	2M	0.5	0.207
50	3M	0.5	0.203
50	4M	0.5	0.201
50	5M	0.5	0.200

Table 2.4 The effect of 0.5% UO_2 on the absorbance of palladium

$[Pd^{2+}]$/ppm	Pd : Sn ratio	[HCL]/M	Absorbance
30	1:0	1M	0.130
30	1:5	1M	0.132
30	1:10	1M	0.131
30	1:0	3M	0.125
30	1:5	3M	0.125
30	1:10	3M	0.126
30	1:0	5M	0.120
30	1:5	5M	0.119
30	1:10	5M	0.120

Table 2.5 The effect of hydrochloric acid and stannous chloride on the absorbance of palladium solutions

The above findings are in agreement with those of Harrington [79] who found that a mole ratio of tin to palladium up to 500 moles does not affect the absorbance of palladium. A depression of the palladium signal is once again evident in going from 1 to 5M HCL but this was compensated for by matching the concentration of acids in the investigated solutions.

We chose to prepare our palladium standards from pure K_2PdCl_4 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. Beer's law was obeyed for 0-70 ppm palladium. A typical calibration curve obtained in this way is shown in Figure 2.2.

Further investigations were carried out to determine whether the 2 noble metals in question mutually interfere with each other in the presence or absence of stannous chloride. 0.2% Lanthanum nitrate was used to suppress interferences in platinum. Results from Table 2.6 show that no mutual or other interferences were

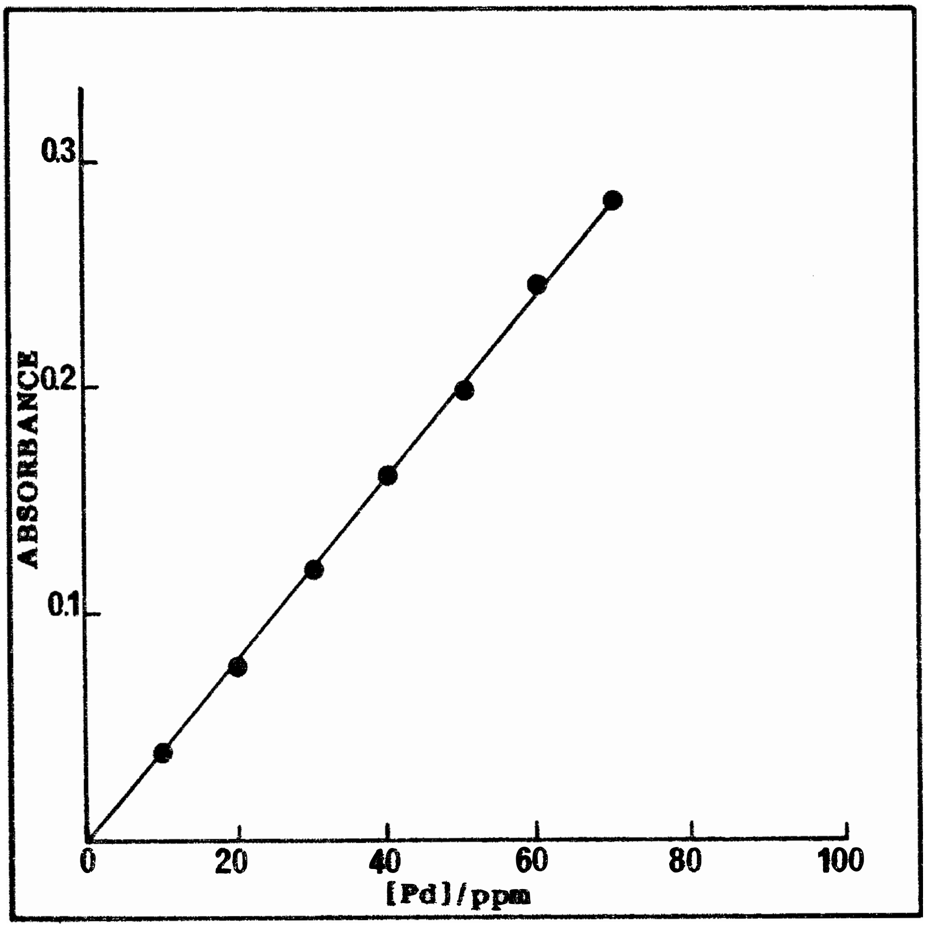


Figure 2.2 A calibration curve of palladium in 1.4M HCL with stannous chloride (Sn:Pd ratio = 10)

found in the presence or absence of stannous chloride in platinum-palladium-tin solutions of 1.5M with tin:platinum/ palladium ratios of 5.

The method developed above for the determination of platinum and palladium in the presence of each other and stannous chloride by AAS was used later for the analysis of these two noble metals in the aqueous phase after their separation by solvent extraction.

[Pt]/ppm	10	21	40	50	60	70
Absorbance						
Pt	0.013	0.026	0.051	0.065	0.077	0.090
Pt+Pd[a]	0.012	0.026	0.051	0.065	0.078	0.091
Pt+Pd+Sn[b]	0.012	0.027	0.052	0.065	0.078	0.091

[Pd]/ppm	5	11	22	27	33	38
Absorbance						
Pt	0.014	0.029	0.058	0.071	0.086	0.101
Pt+Pd[a]	0.014	0.029	0.057	0.071	0.086	0.100
Pt+Pd+Sn[b]	0.014	0.029	0.058	0.072	0.088	0.100

a Pt:Pd molar ratio 1:1

b Pt:Pd molar ratio 1:1; Pt, Pd : Sn ratio 1:5

Table 2.6 The effect of palladium (platinum) and tin on the absorbance of platinum (palladium) in 1.4M HCL with 0.2% $La(NO_3)_3$

Typical calibration curves obtained for platinum and palladium in this way are shown in Figure 2.3.

2.1.3 *Atomic Absorption Determination of Tin*

The determination of tin in hydrochloric acid solutions can be done relatively easily by the atomic absorption method. A strongly reducing air-acetylene flame is required and was used in this work since it provides a medium for tin atomic absorption which is considerably less subject to interferences compared with for example the nitrous oxide-acetylene and air-hydrogen flames. The 286.3 nm line was used for all measurements.

Figure 2.4 shows a typical calibration curve obtained using platinum-containing tin standards in 2.4M HCL.

Yates [50] showed that platinum does not interfere in the determination of tin by the atomic absorption method since the concentration of tin could be accurately determined in the presence of platinum. Results in Table 2.7 show that palladium also does not interfere in the determination of tin by atomic absorption in hydrochloric acid solutions.

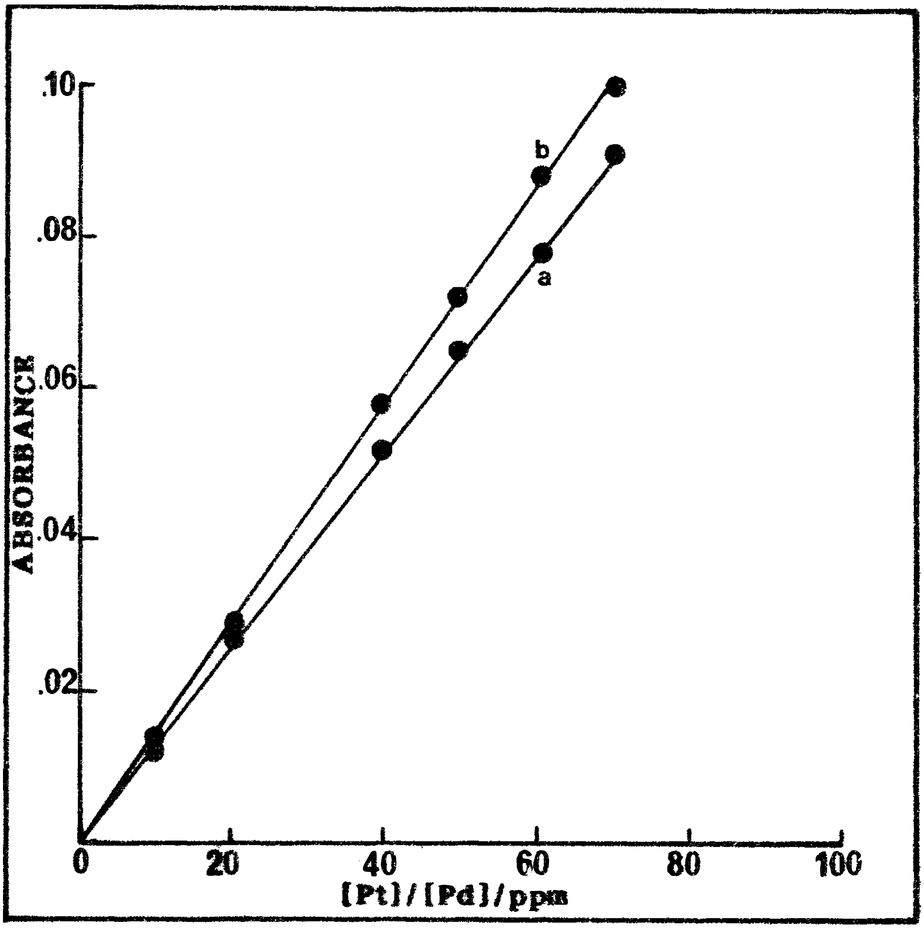


Figure 2.3 Calibration curves for (a) platinum and (b) palladium in the presence of each other with stannous chloride and 0.2% $La(NO_3)_3$ in 1.4M HCL (Sn:Pd/Pt ratio = 5)

Pd : Sn ratio	[Sn] taken/ ppm	[Sn] found/ ppm	Relative percentage error
1:5	82.3	82.2	0.1
1:7	115.7	116.0	0.3
1:9	147.9	147.0	0.6
1:10	164.6	164.0	0.4
1:12	196.7	196.0	0.4

Table 2.7 The effect of palladium on the determination of tin in 2.4M HCL

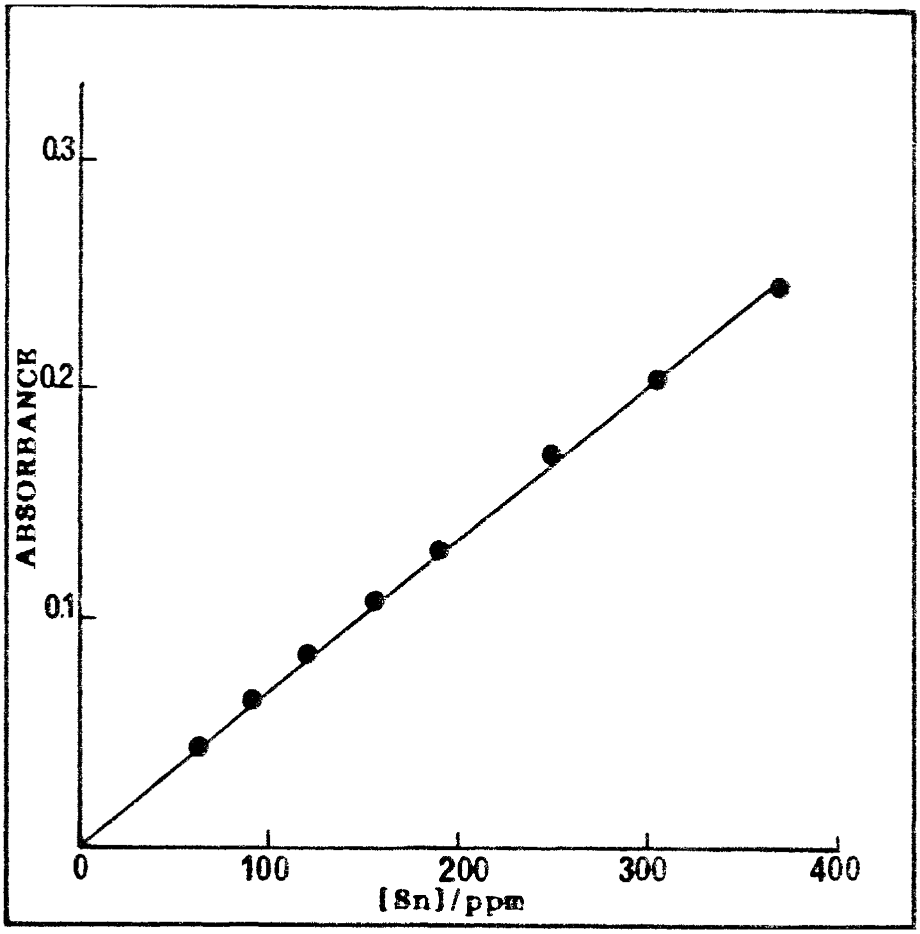


Figure 2.4 A calibration curve for tin in 2.4M HCL solution

2.1.4 *Potassium Iodate Oxidations*

The titrimetric determination of tin(II) in hydrochloric acid by oxidation with potassium iodate is a well-documented method [80-82]. Potassium iodate solution reacts quantitatively with tin(II) in the presence of concentrated hydrochloric acid, according to the overall equation:

$$2SnCl_2 + KIO_3 + 6HCL \rightleftarrows 2SnCl_4 + KCl + ICl + 3H_2O$$

$$\text{Thus } 1KIO_3 = 2Sn$$

The procedure involves the use of an immiscible organic solvent, such as chloroform or carbon tetrachloride with the end point of the titration being marked by the disappearance of the last trace of violet colour from the organic solvent. This colour is due to iodine formed during the reaction as a by-product. Iodine monochloride (ICl) is not extracted and imparts a pale yellowish colour to the aqueous phase. The main disadvantage is the inconvenience of vigorous shaking with the organic solvent in a stoppered vessel after each addition of the reagent near the end point. This method is very useful in that it can be used to determine accurately the exact concentration of Sn^{2+} present.

Because of the rapid ease with which tin(II) is oxidised to tin(IV) by oxygen in the air, extreme precautions were taken to perform all the titrations under pure, deoxygenated nitrogen.

Vogel [82] reports that the optimum acidity for a reasonably rapid reaction during the titration varies from one reductant to another within the range 2.5 - 9M hydrochloric acid : in many cases the concentration of acid is not critical. Although investigations were not carried out to determine the effect of acid concentration on the titration, we arbitrarily chose them to be between 4.5 and 5.5M HCL for our titrations.

In our work, potassium iodate oxidations were used to determine the exact percentage of Sn^{2+} present in the freshly prepared stannous chloride solutions. Typical results are shown in Table 2.8

Standard solution taken/ mmol	Total oxidisable species expected/ mmol	Volumes KIO_3 used/mmol	Mean Titre ml/KIO_3	Total oxidisable species found/ mmol	Percentage Sn^{2+}
0.256	0.256	1.82			
			1.83	0.236	92%
		1.84			
0.163	0.163	2.40			
			2.40	0.156	96%
		2.40			
0.163	0.163	2.30			
			2.30	0.150	92%
		2.30			

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

2.2 The extraction of tin from hydrochloric acid solutions by isobutylmethylketone-hexane mixtures

The extraction of tin from hydrochloric acid solutions into certain organic solvents, for example diethyl ether [83, 84], tributyl phosphate (TPB) [85] and isobutylmethylketone [86, 87] has been studied. Analysis of the literature data regarding the detailed study of the extraction of tin(II) and tin(IV) undoubtedly indicates a similarity in the extraction of tin(II) and tin(IV). However, tin(II) is known to be unstable in solutions and to be readily oxidised to tin(IV) by atmospheric oxidation. In their studies on the extraction of bivalent tin in an atmosphere of argon, Levin and Tarasova [88] found that the extraction of tin(II) and tin(IV) differred greatly, which, according to other authors show almost identical behaviour. They therefore concluded that the previous authors mentioned [87] had extracted tin(IV) in both cases.

In our investigations we determined the extractability of tin(II) in an atmosphere of nitrogen and in the absence of platinum and palladium into MIBK-hexane mixtures (v/v) at various acid concentrations. We considered this to be an important factor in our attempt to explain the observed stoichiometry of the extract-

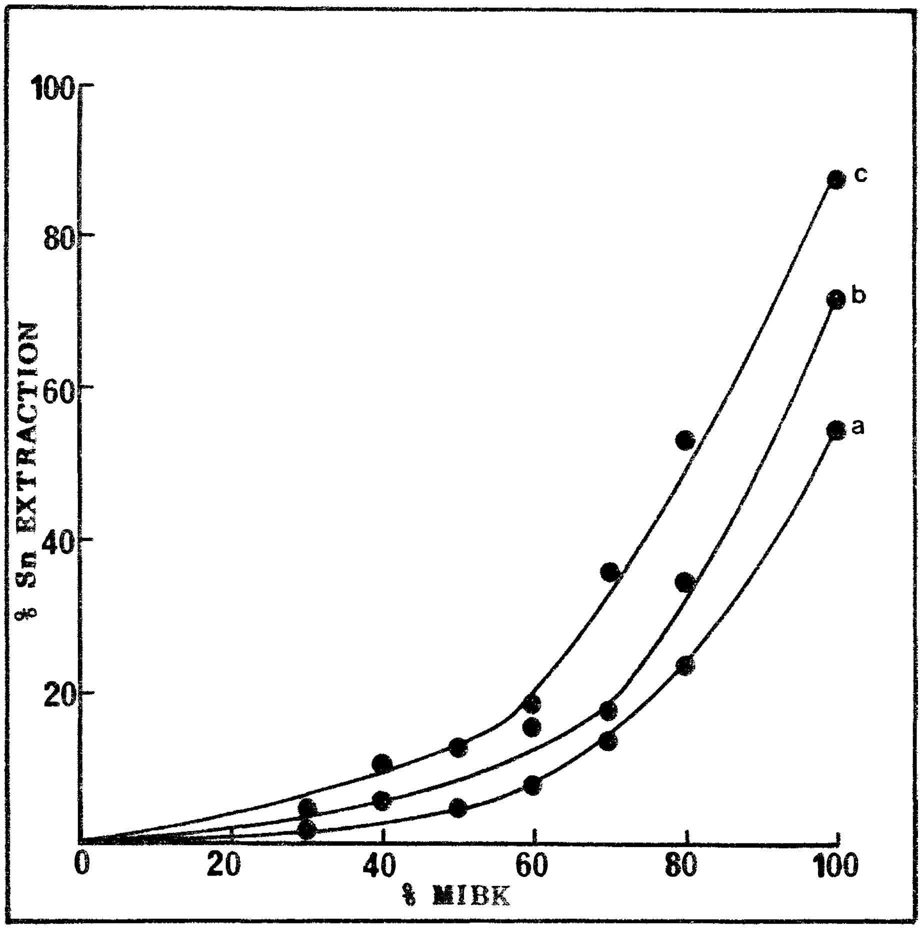


Figure 2.5 The extraction of tin(II) from (a) 1.4M (b) 2.4M and (c) 3.4M HCL solutions as a function of % MIBK

ed platinum-tin chloride complex(es) since tin (in the absence of platinum) is extracted probably in the form $SnCl_3^-$ and $SnCl_4^{2-}$ with increasing amounts of MIBK in hexane. These extractions were performed in 1.4, 2.4 and 3.4M HCL using an extraction time of 10 minutes. Figure 2.5 shows the percentage tin extraction as a function of % MIBK in hexane.

It is evident that very little tin is extracted into the organic phase at less than 50% MIBK, but a significant increase in the extraction of tin is observed with increasing amounts of MIBK. The amount of tin extracted is also dependant upon the acid concentration with more tin being extracted at higher acid concentrations.

2.3 Ultraviolet - visible spectrophotometry

Most of the analytical spectrophotometrical methods of determining the noble metals utilise coloured complex compounds of these elements [89]. The coloured products obtained from noble metals on treatment with tin(II) chloride or tin(II) bromide have been used extensively for the spectrophotometric determination of these metals.

2.3.1 *Equilibration of the Aqueous Phase for Platinum*

Tin(II) chloride has long enjoyed use as a colorimetric reagent for platinum [90]. Its reaction with platinum to form brightly coloured compounds was first observed by Wöhler [91] and has subsequently been used for determining small amounts of platinum. Since then many authors have made detailed spectrophotometric studies of the platinum-tin(II) chloride system in an attempt to determine the reaction stoichiometry in the formation of the coloured products in solution.

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.

The UV-visible absorption spectra of freshly prepared aqueous solutions containing a tin : platinum ratio of 2 at various acid concentrations were determined as a function of time by Yates [50]. Equilibrium was reached in 10 minutes for solutions of 1M hydrochloric acid concentration and repeated scans every 10 minutes from 0 - 40 minutes showed that the spectrum did not change significantly.

At 1.5M hydrochloric acid concentration, however, equilibrium was reached after 20 minutes and no significant change in the spectrum was observed from 20 - 50 minutes. Molar extinction coefficients and absorption maxima obtained at these acid concentrations are tabulated in Table 2.9

Acid Concentration M	Absorption Maxima nm	Molar extinction coefficients $cm^2\ mol^{-1}$
1	373	8.52×10^6
	431	3.71×10^6
	506	1.63×10^6
1.5	374	3.79×10^6
	438	1.75×10^6
	517	7.50×10^5

Table 2.9 Absorption maxima and molar extinction coefficients for tin : platinum ratio of 2 at various acid concentrations

The spectrophotometric determination of mixed platinum and tin solutions at higher acid concentrations was found to be somewhat complicated, most probably due to the rapid oxidation of tin(II) at the higher acidities. The colour intensity of solutions at 6M HCL was observed to decrease rapidly with time. Absorption spectra obtained appeared to be complicated in that certain absorbances increased with time, whereas others decreased accordingly; no steady state was reached.

An initial equilibration period of 20 minutes was therefore allowed for the Pt-Sn complex before each extraction experiment.

2.3.2 *Equilibration of the Aqueous Phase for Palladium*

Ayres and Alsop [32] observed that when tin(II) chloride was added to palladium chloride in hydrochloric acid solution an intense orange-red colour developed with the first few drops of the reagent; on further addition of tin(II) chloride, the colour changed to yellow-green, then to nearly black, and finally to dark green. When an excess of tin(II) chloride was added rapidly, only the dark green colour was observed. This green colour (λ max 635 nm) which attained its maximum colour intensity after 20 minutes standing at room temperature, was found to be suitable for spectrophotometric application in the range of about 8 to 32 ppm palladium.

The UV-visible spectra of freshly prepared aqueous phase solutions containing Pd(II):Sn(II) ratios of 1:10 at various acid concentrations were determined as a function of time. It was found that for hydrochloric acid concentrations of 1.5, 1.8 and 2.4M a steady state was reached after ± 15 minutes. Repeated scans every 5 minutes from 15 to 35 minutes showed that the spectrum did not change significantly, thus an initial equilibration period of 15 minutes was allowed for the Pd-Sn complex before addition of the organic phase.

Considerable changes in the absorption spectra of palladium(II) chloride occur after the introduction of tin(II) chloride. The visible absorption spectra at all acid concentrations show 2 maxima at 410 and 630 nm which shows that complex formation takes place. (Figures 2.6, 2.7 and 2.8).

These maxima are reported to be characteristic of the yellow and green palladium-tin complexes [92, 93]. At higher acidities the peaks at 410 and 630 nm were observed to decrease in height reaching a steady state at about 2.4 M HCL. Molar extinction coefficients at the different acid concentrations for the equilibrated state are given in Table 2.10.

Acid Conc M	Absorption Maxima nm	Molar extinction coefficients $cm^2\ mol^{-1}$
1.5	410	2.77×10^5
	630	3.90×10^4
1.8	410	2.27×10^5
	630	1.77×10^4
2.4	410	2.23×10^5
	630	1.42×10^4

Table 2.10 Absorption maxima and molar extinction coefficients for tin : palladium ratio of 10 at various acid concentrations.

On standing the transmittance of the Pd-Sn solutions decreased over the entire spectrum, indicating the presence of light scattering by colloidal particles. This corresponds with the formation of a very fine grey-black precipitate which, with time, settled to the bottom of the cuvette.

This precipitate, according to Zayats [36], is an unstable palladium hydrosol formed as a result of the reaction:

$$Pd^{2+} + Sn^{2+} \rightleftarrows Pd^{o} + Sn^{4+}$$

2.4 Extraction Times for Platinum and Palladium

Experiments were performed in order to determine the effect of extraction time allowed on the extraction efficiency of platinum and palladium.

Figure 2.9 clearly illustrates that % extraction of platinum and tin remains more or less constant with time, indicating that the

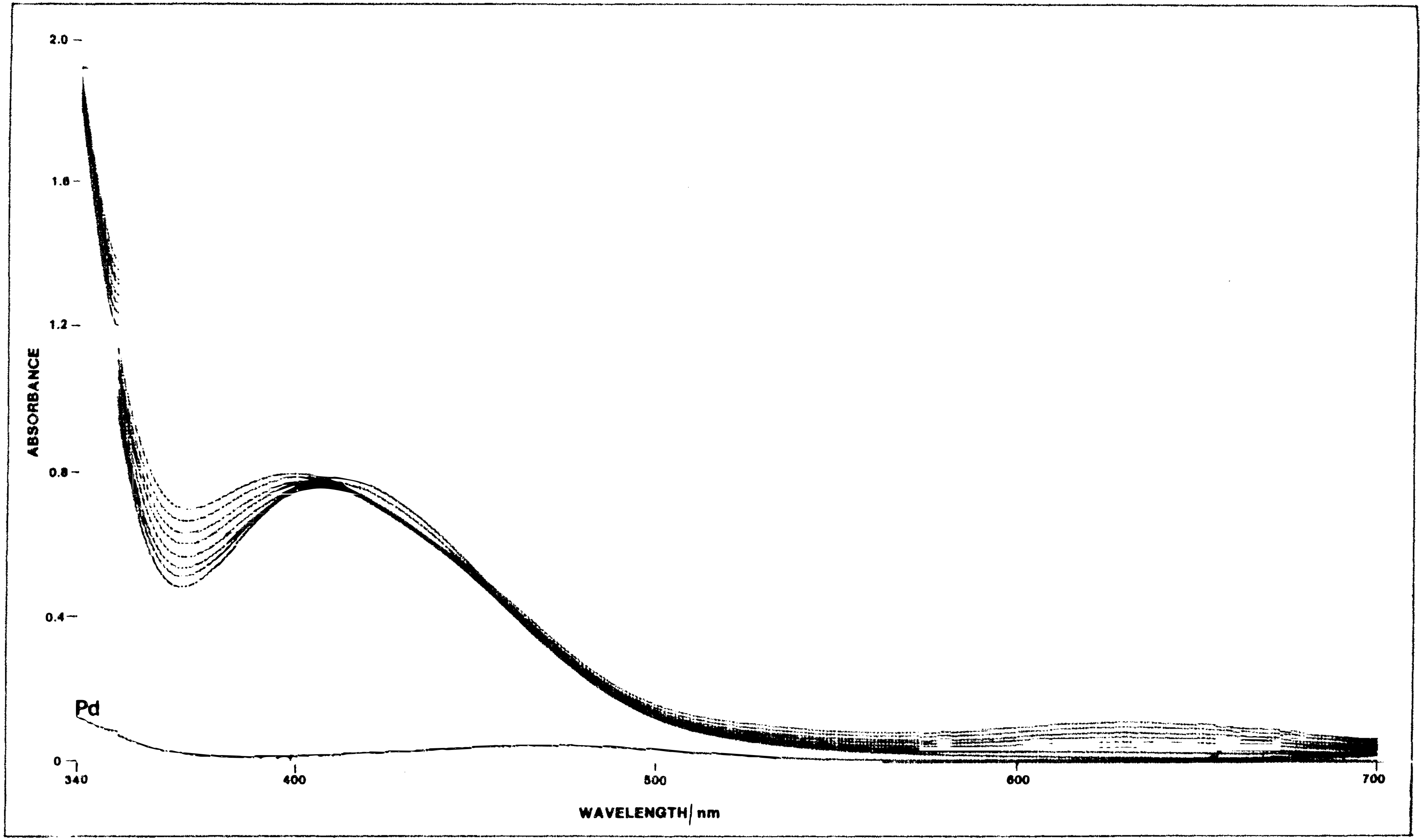


Figure 2.6 Visible absorption spectra for solutions of Sn(II):Pd(II) ratio of 10 at 1.4M HCL. Repeated scans every 5 minutes for 5 - 35 minutes.

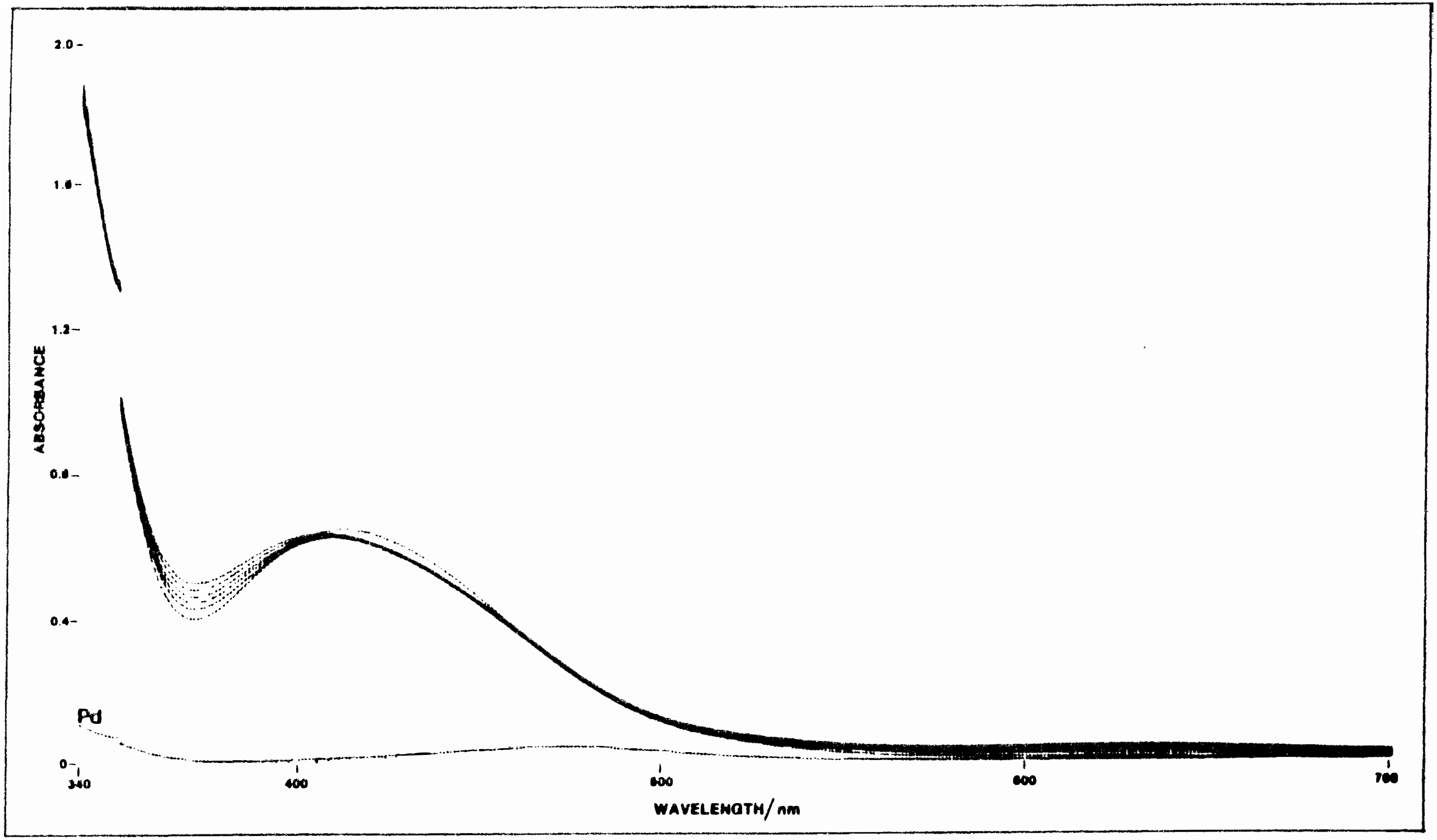


Figure 2.7 Visible absorption spectra for solutions of Sn(II):Pd(II) ratio of 10 at 1.8M HCL. Repeated scans every 5 minutes for 5 - 35 minutes.

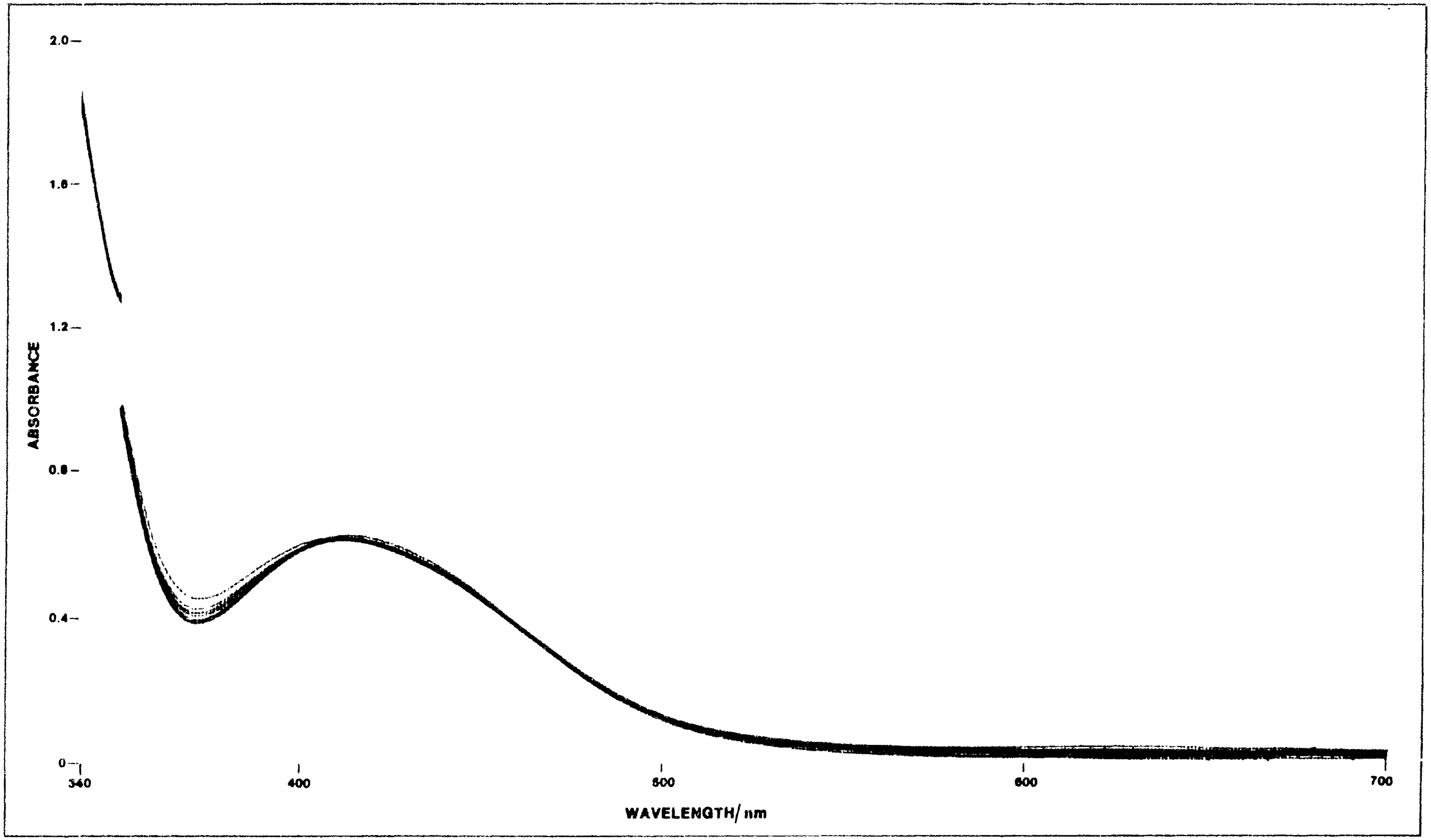


Figure 2.8 Visible absorption spectra for solutions of Sn(II):Pd(II) ratio of 10 at 2.4M HCL. Repeated scans every 5 minutes for 5 - 35 minutes

extraction process is rapid. Experiments were performed at 2.4M HCL using a 1:5 Pt:Sn ratio in 40% MIBK. Extraction times chosen were from 2 - 15 minutes. We arbitrarily chose our platinum extraction time to be 10 minutes.

The above experiment was repeated for palladium at 1.4M and 2M HCL in 100% MIBK using a 1:10 Pd:Sn ratio. Extraction times chosen were from 2 - 15 minutes. Figure 2.10 shows a plot of % palladium extracted as a function of time. As was the case for

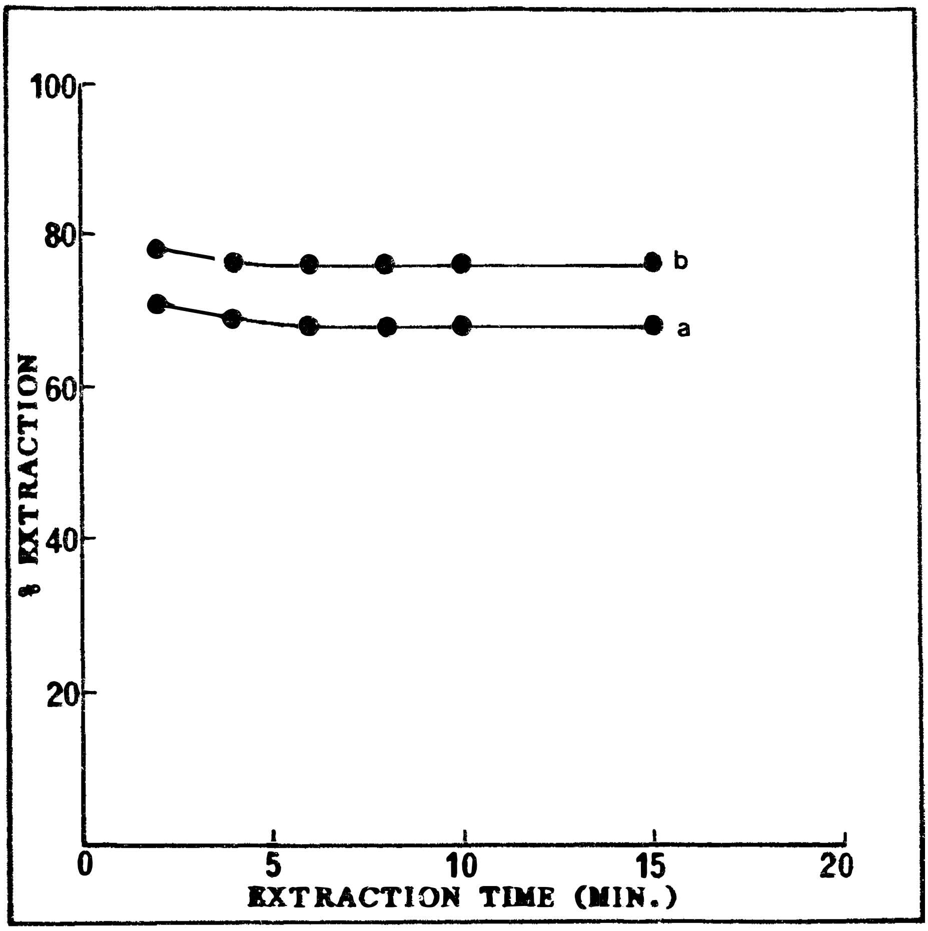


Figure 2.9 Variation of percentage extraction of (a) tin and (b) platinum from 2.4M HCL solutions with extraction time at Sn(II):Pt(II) ratio of 5

platinum, rapid extraction of palladium occurs and we chose an extraction time of 5 minutes for our palladium extraction experiments.

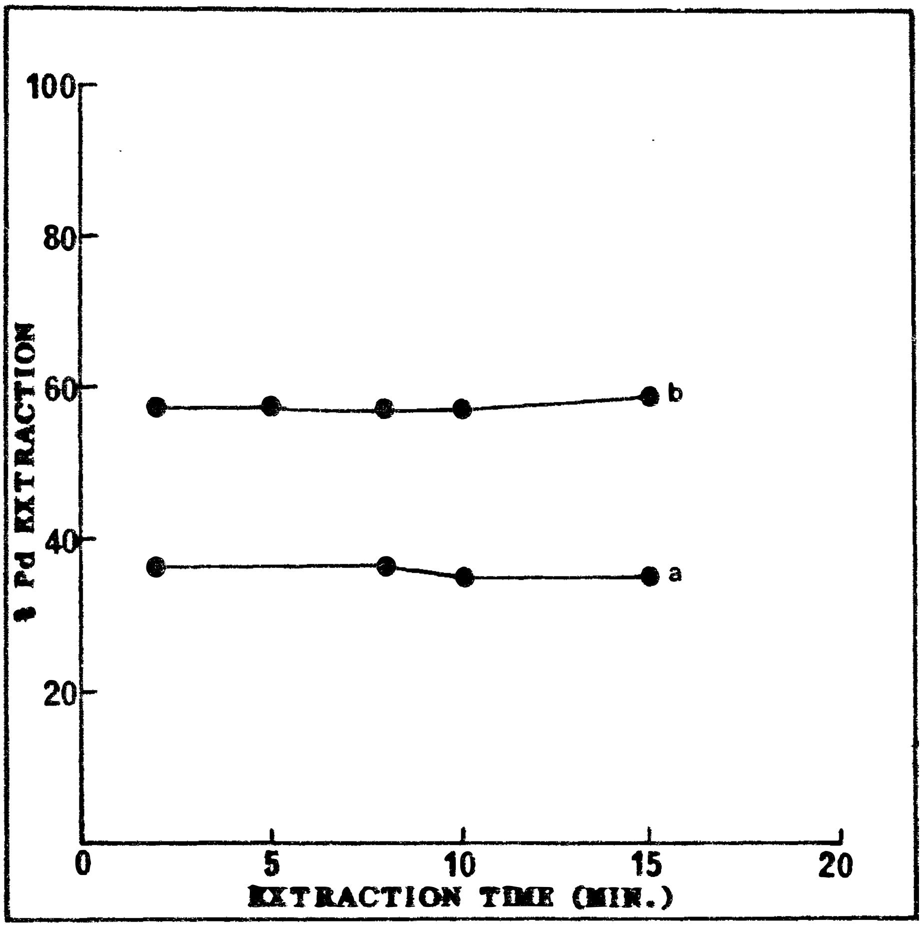


Figure 2.10 Variation of percentage extraction of palladium from (a) 1.4M and (b) 2M HCL solutions with extraction time at Sn(II):Pd(II) ratio of 10

CHAPTER 3

CHAPTER 3

3. SOLVENT EXTRACTION OF PLATINUM

Having established equilibration and extraction times for platinum and devised suitable analytical methods for the accurate determination of both platinum and tin in the aqueous phase, we proceeded to examine in detail the extraction behaviour of platinum complexes of $SnCl_3^-$ from aqueous hydrochloric acid solutions using MIBK/hexane mixtures as extractants. Our objective was to establish which parameters influence the efficiency of extraction and to what extent platinum and palladium may be separable by this method. Strict precautions were taken to perform all the extractions under an inert atmosphere of nitrogen in order to prevent the oxidation of stannous chloride in solution. Detailed experimental procedures are outlined in Section 7.8 of Chapter 7.

3.1 The Effect of Sn(II):Pt(II) ratio

Preliminary qualitative results showed that platinum is virtually quantitatively extracted into pure MIBK from 1.0 to 3.0 M HCL solutions containing $PtCl_4^{2-}$ and $SnCl_2$ if the Sn(II):Pt(II) molar ratio is > 4. However, if MIBK is mixed with hexane the distribution coefficient of platinum decreases to zero in the case of pure hexane as organic phase.

A study of the effect of increasing tin(II) concentration on the extraction of the 'red complexes' from aqueous hydrochloric acid phases into MIBK/hexane mixtures was undertaken. Two factors must however be recognised:

(i) tin is extracted (in the absence of platinum) with increasing amounts of MIBK in hexane

(ii) platinum appears to be extractable in complexes in which not all Cl^- ligands have been replaced by $SnCl_3^-$, although the efficiency of extraction increases as the platinum becomes co-ordinatively saturated with respect to the $SnCl_3^-$ ligands (i.e. all Cl^- replaced by $SnCl_3^-$).

Hydrochloric acid solutions containing $PtCl_4^{2-}$ and the desired amount of $SnCl_2$ were equilibrated for 20 minutes, followed by extraction with mixtures of MIBK in hexane from 0-100% MIBK. The separate phases were then analysed by AAS and percentage platinum and tin extracted was determined by comparison with a blank consisting of an aqueous phase only. Initially, the blank comprised of an aqueous phase containing Sn:Pt in the appropriate ratio and an organic phase of hexane only. In separate experiments mass balance was demonstrated (see Appendix 1). Three sets of extractions at 1.4, 2.4 and 3.4 M HCL were performed as described, with appropriate tin(II) and platinum(II) concentrations chosen for the various ratios. Figure 3.1 shows the results of these experiments at the different acid concentrations. In the absence of $SnCl_2$ i.e. at a Sn:Pt ratio of 0, no $PtCl_4^{2-}$ is extracted by pure MIBK. It is evident that the presence of increasing amounts of stannous chloride dramatically increases the percentage platinum extracted into the organic phase.

Both the amount of platinum and tin extracted was found to be dependant on the Sn(II):Pt(II) ratio in the aqueous phase before extraction. A definite trend is evident in the case of platinum with increased amounts of platinum being extracted with an increase in the Sn(II):Pt(II) ratio in the aqueous phase. Maximum extraction for each particular Sn(II):Pt(II) ratio was found to occur at 100% MIBK. It is also evident that percentage extraction of platinum increases significantly above 30% MIBK.

The percentage tin extracted shows a general increase with increasing Sn(II):Pt(II) ratios up to a ratio of 5, in parallel with the amount of platinum extracted. However, in contrast to platinum, percentage extraction of tin is generally not comparable since increased amounts of tin were added to obtain the desired Sn(II):Pt(II) ratios in the aqueous phase initially. Thus, although the percentage tin extracted at 60% MIBK for Sn(II):Pt(II) ratios of 10 in 3.4M HCL correspond to ≈ 48% while at a ratio of 2 approximately 72% extraction is observed, the actual amount of tin extracted at the higher ratios is actually

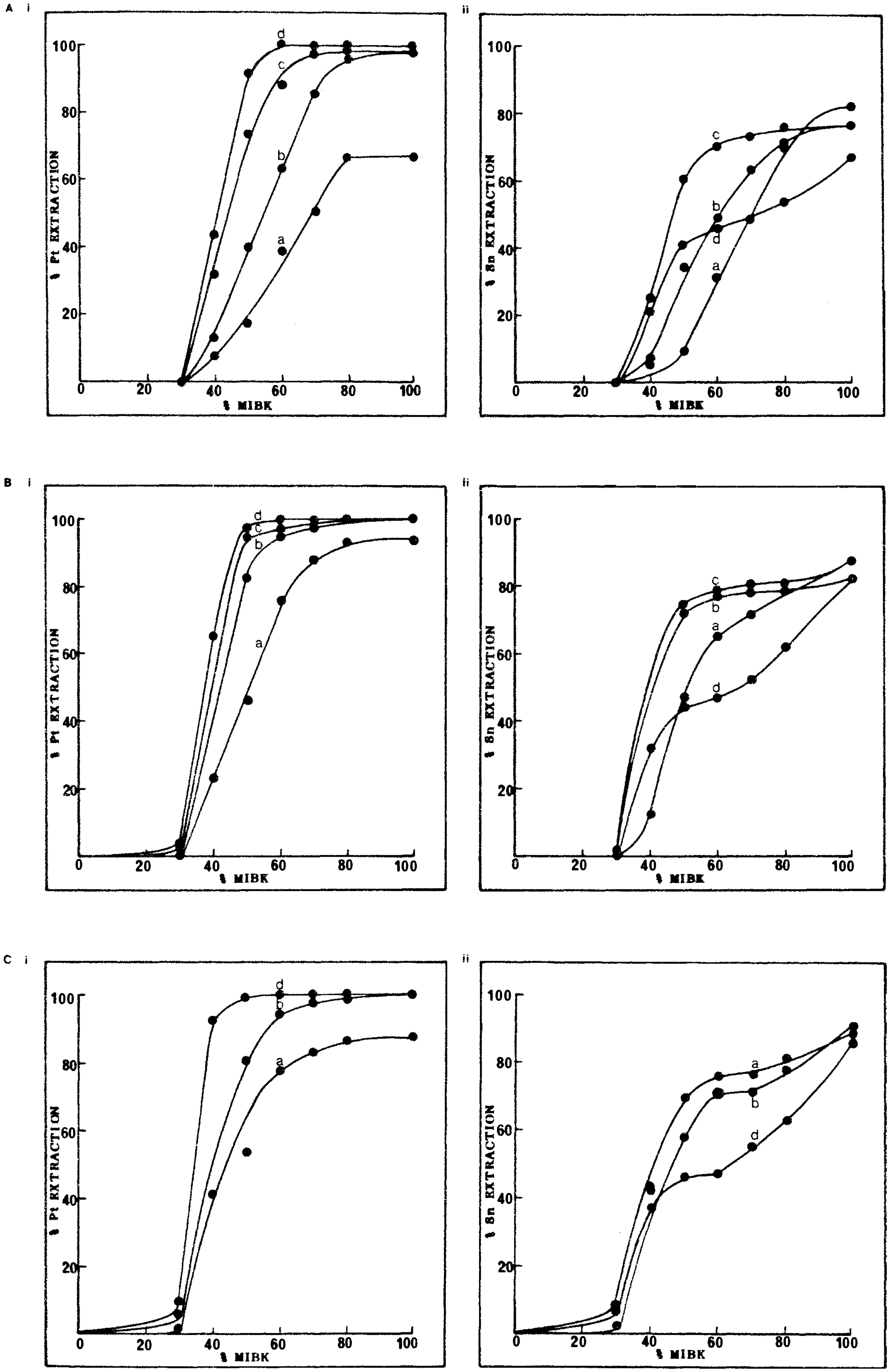


Figure 3.1 The variation of percentage extraction of (i) platinum and (ii) tin from
(A) 1.4M
(B) 2.4M
(C) 3.4M
HCL solutions with % MIBK at Sn(II):Pt(II) ratios of (a) 2 (b) 4 (c) 5 and (d) 10

much higher due to its higher concentration in the aqueous phase. The extraction of tin was also observed to 'level off' at Sn(II):Pt(II) aqueous phase ratios of ≥ 5, indicating that the 5:1 Sn:Pt ratio is significant.

The distribution coefficients (DC) of platinum and tin as a function of percentage MIBK in the organic phase were determined at the various acid concentrations. Results obtained are shown in Figure 3.2 as a plot of log DC vs % MIBK.

A number of interesting observations were made during the course of these extractions. The rate of formation of the red colour was found to be dependant on the Sn(II):Pt(II) ratio in the aqueous phase. At high Sn:Pt ratios the colours form rapidly and are generally more intense, increasing from light orange-red at low Sn(II):Pt(II) ratios to a characteristic deep, dark-red.

Our extraction experiments also showed that the amount of platinum extracted from red solutions containing fixed Sn(II):Pt(II) ratios depends on the percentage MIBK in the organic phase. Thus for a fixed Sn(II):Pt(II) ratio the intensity of the red colour in the aqueous phase changes from its original deep-red to light yellow-orange to almost colourless on extraction. This was in parallel with the observed colour intensities of the organic phases which varied from colourless (0% MIBK) to orange (50% MIBK) to dark orange-red (100% MIBK).

Figure 3.3 shows how the percentage platinum extracted varies with the Sn(II):Pt(II) ratio in the aqueous phase at fixed percentages of MIBK.

A definite increase in the percentage platinum extracted is evident between Sn:Pt ratios of 4 and 5, but no significant increase in extraction is observed between Sn:Pt ratios of 5 and 10. This suggests that at a Sn:Pt ratio of 5:1 platinum is co-ordinatively saturated as far as the $SnCl_3^-$ ligands are concerned and any further increase in tin (II) concentration has no significant effect on the extraction.

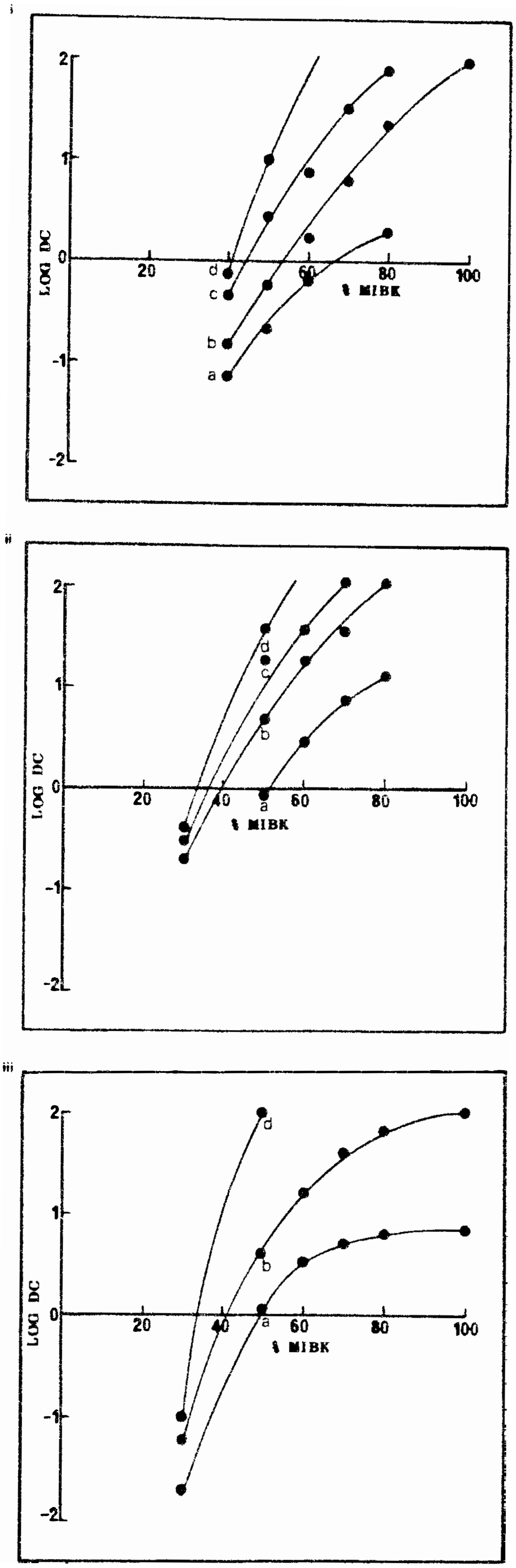


Figure 3.2 The dependence of the distribution coefficients of platinum on the concentration of MIBK in the organic phase after extraction from (i) 1.4M (ii) 2.4M and (iii) 3.4M HCL solutions at Sn(II):Pt(II) ratios of (a) 2 (b) 4 (c) 5 and (d) 10

It is evident that percentage platinum extracted shows a general increase with increased Sn(II):Pt(II) ratio, a trend which is paralleled by observing the increased colour intensities of the organic phases. At high Sn(II):Pt(II) ratios the colours were generally more intense increasing from light-yellow through orange to a dark red-orange. It is evident that provided sufficient tin(II) is present (Sn(II):Pt(II) ≥ 5) platinum is quantitatively extracted by > 70% MIBK.

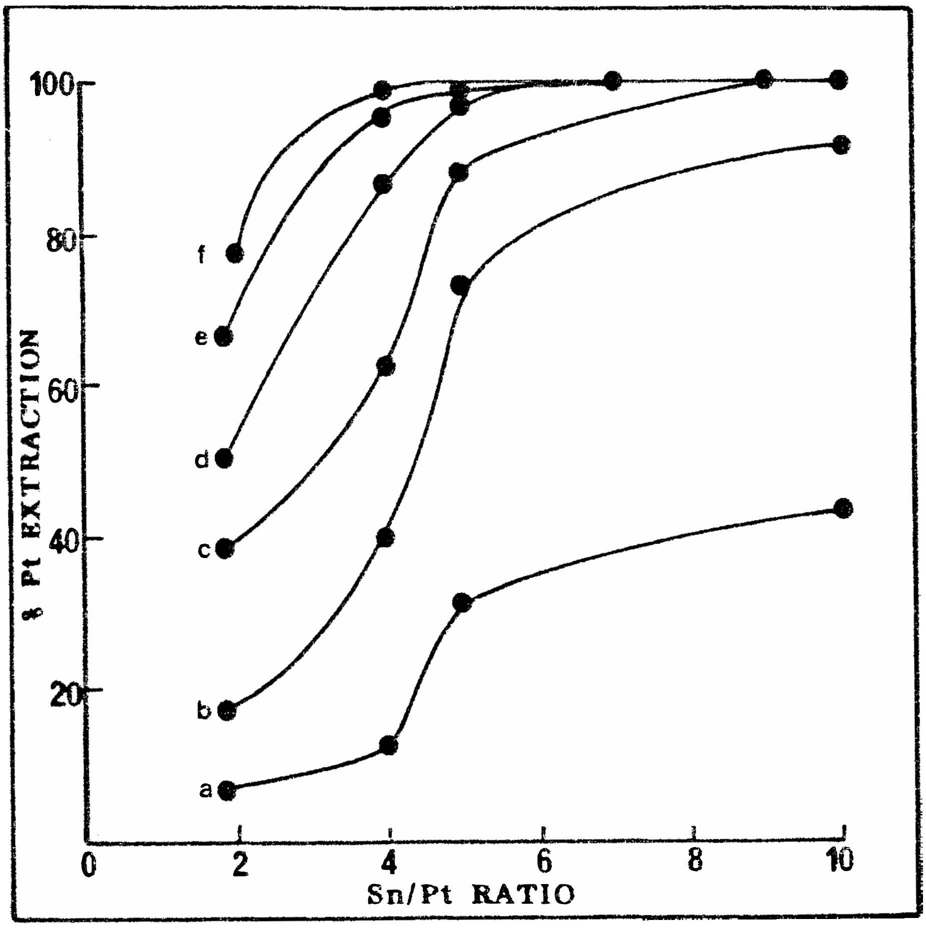


Figure 3.3 The effect of Sn(II):Pt(II) ratio on the extraction of platinum from 1.4M HCL solutions by (a) 40 (b) 50 (c) 60 (d) 70 (e) 80 and (f) 100% MIBK

3.2 The Effect of Hydrochloric Acid Concentration

Results shown in Figure 3.1 indicated that variations in acid concentration affected the extraction process. Thus experiments were performed to determine the effect of HCL concentration on percentage platinum and tin extraction into 40% MIBK in hexane at various Sn(II):Pt(II) ratios. HCL concentrations chosen were from 1.5 to 4M and precautions were taken to exclude air at all times. The required HCL concentrations were made up by adding appropriate amounts of concentrated HCL to successive extraction tubes.

Figure 3.4 shows that variations in acid concentrations affects the extraction quite significantly. Percentage extraction of platinum generally increases with increased acid concentration with maximum extraction occuring at 4M HCL for all Sn(II):Pt(II) ratios. The colours of the organic phases were observed to parallel this trend, being more intense than at lower acid concentrations. At high Sn(II):Pt(II) ratios, the observed increase in percentage platinum extracted with increased HCL concentrations is more pronounced than that at lower Sn(II):Pt(II) ratios.

The concentrations of the hydrogen and chloride ions increase with an increase in HCL concentration. The observed effect of HCL concentration made us curious as to whether the H^+ and Cl^- ions would have competing or opposing effects on the extraction of platinum. Studies to determine the effects of these two ions on the extraction process were therefore undertaken.

3.3 The Effect of Hydrogen Ion Concentration

Experiments to determine the effect of hydrogen ion concentration on the extraction were performed by adding portions of freshly prepared HCL-$HClO_4$ solutions to successive extraction tubes to give the desired range of hydrogen ion concentrations. Sodium salts of platinum were used for these extractions since the use of their appropriate potassium counterparts would have resulted in the precipitation of potassium perchlorates. The exact $[H^+]$ under which the extractions were carried out was determined by standardising against sodium tetraborate.

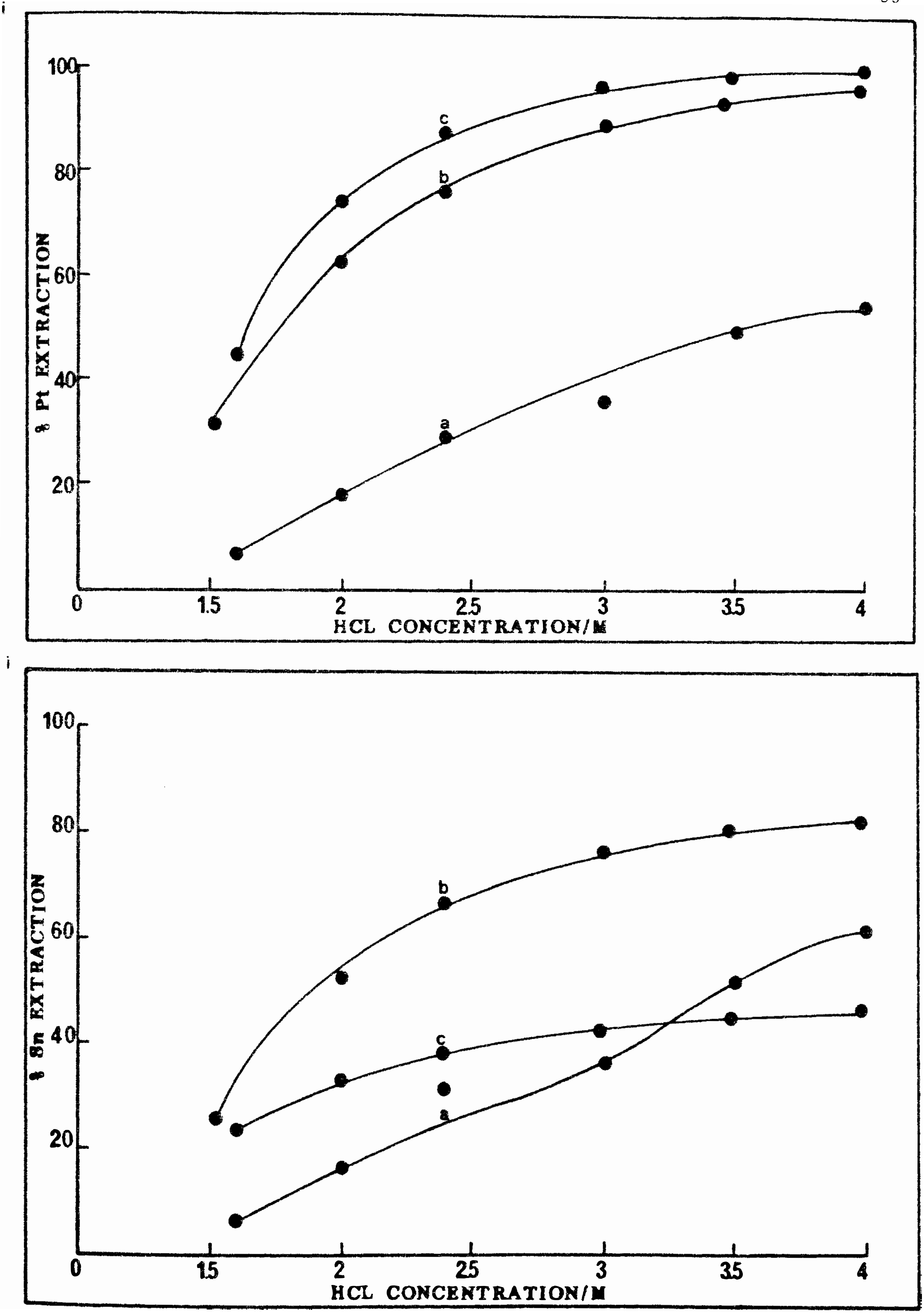


Figure 3.4 The effect of hydrochloric acid concentration on the extraction of (i) platinum and (ii) tin by 40% MIBK at Sn(II):Pt(II) ratios of (a) 2 (b) 5 and (c) 10

Figure 3.5 shows the variation of percentage platinum and tin extracted with H^+ concentration at various ratios. It is clearly evident that percentage extraction of platinum is dependant to a large extent on the hydrogen ion concentration, increasing with increased H^+ concentration. Similar trends were obtained when investigating the effect of HCL concentration on the extraction of platinum suggesting that the hydrogen ion has an overwhelming influence on the extraction process.

3.4 The Effect of Chloride Ion Concentration

Experiments performed to determine the effect of chloride ion concentration involved the addition of increasing amounts of ammonium chloride (NH_4Cl) to the extraction tubes containing the aqueous phases at fixed Sn(II):Pt(II) ratios. The extraction tubes were tightly stoppered and the NH_4Cl dissolved by gentle shaking prior to extraction. The colours of the aqueous phases were observed to vary from dark-red (*ca* 1.4M Cl^-) to light orange-yellow (*ca* 4M Cl^-) with an increase in chloride ion concentration, especially at low Sn:Pt ratios. It is probable that this is presumably due to the predominant existence of the $SnCl_4{}^{2-}$ species at high chloride concentrations which is not known to form complexes with $PtCl_4{}^{2-}/PtCl_6{}^{2-}$, hence resulting in the observed decrease in the intensity of the red colour of the aqueous phases. We therefore predicted that increased $[Cl^-]$ would inhibit the formation of the extractable Pt-Sn complexes resulting in an overall decrease in the extraction of platinum.

Figure 3.6 shows the variation of percentage extraction of platinum and tin with chloride ion concentration. It is evident that increased chloride ion concentration (up to 4M Cl^-) results in a gradual increase in the extraction of platinum. Complete extraction of platinum did not occur at all the Sn:Pt ratios and chloride ion concentrations investigated. The percentage extraction of platinum was substantially less when compared with the amount of platinum extracted over the corresponding range of H^+ and HCL concentrations.

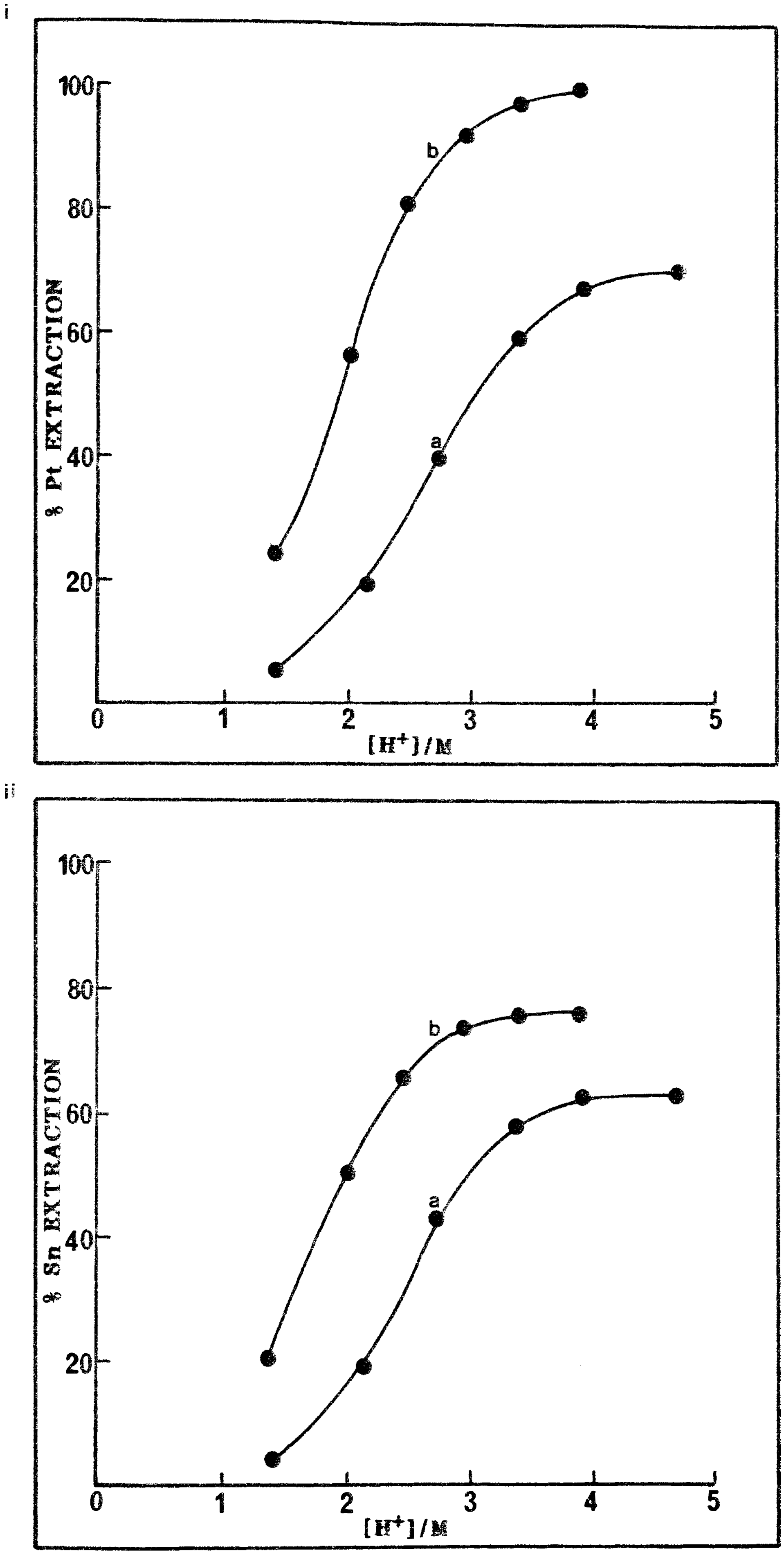


Figure 3.5 The effect of hydrogen ion concentration (at fixed $[Cl^-] = 1.4M$) on the extraction of (i) platinum and (ii) tin by 40% MIBK at Sn(II):Pt(II) ratios of (a) 2 and (b) 5

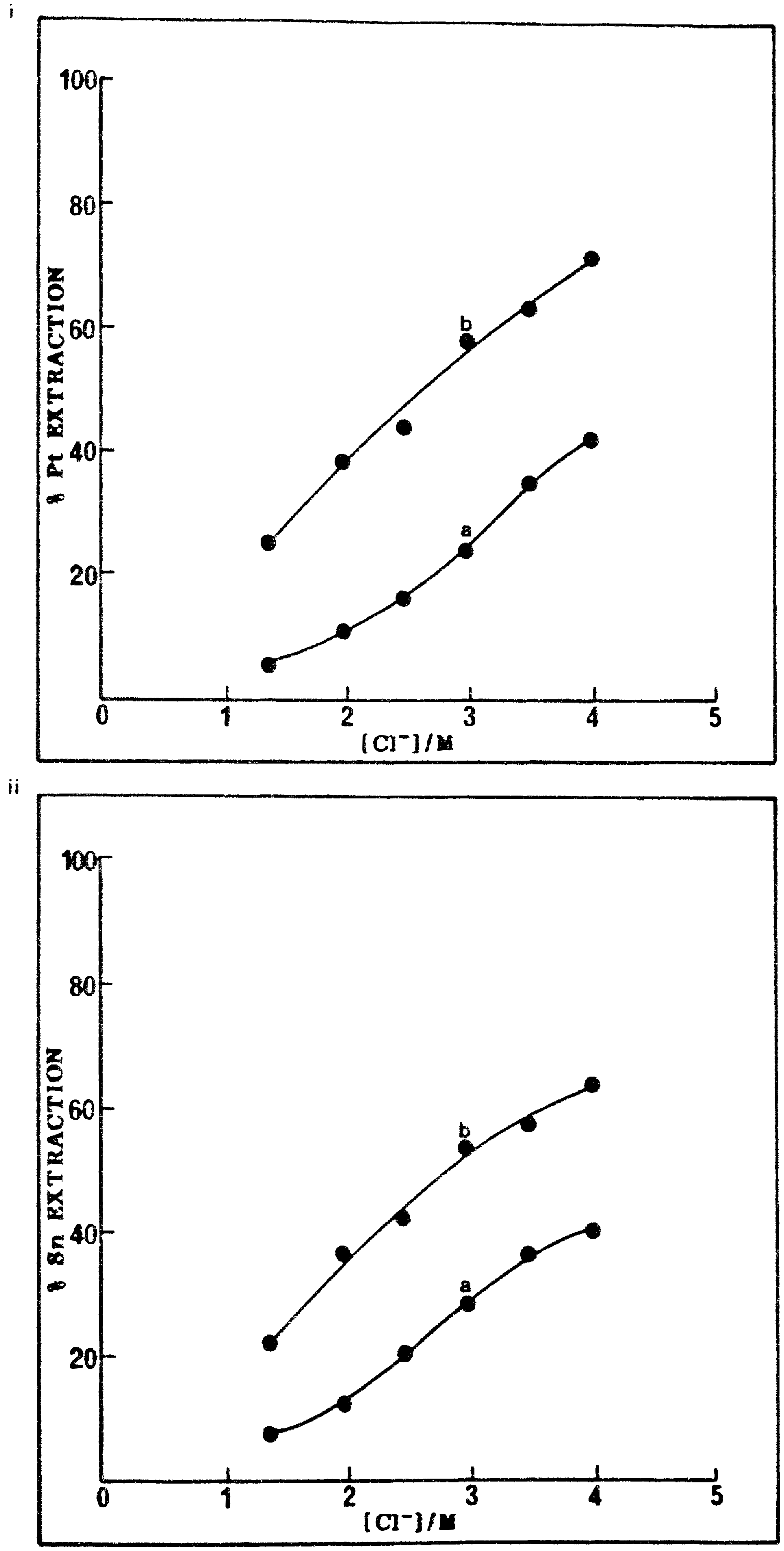


Figure 3.6 The effect of chloride ion concentration (at fixed $[H^+]$ = 1.4M) on the extraction of (i) platinum and (ii) tin by 40% MIBK at Sn(II):Pt(II) ratios of (a) 2 and (b) 5

Figure 3.7 shows the combined effect of HCL, H^+ and Cl^- concentrations on the extraction of platinum at the various Sn:Pt ratios investigated. When comparing the amount of platinum extracted from solutions of variable [HCL] (< 2.4M) with corresponding solutions of variable [H^+] (at fixed [Cl^-] = 1.4M) no significant difference is observed. However, if the [HCL] and [H^+] exceeds 2.4M an additional effect arises. At low Sn:Pt ratios more platinum is extracted from solutions containing high [H^+] (fixed [Cl^-]) than from corresponding HCL concentrations. This is presumably due to the fact that at HCL concentrations greater than 2.4M appreciable amounts of the non-platinum complexing tin species viz. $SnCl_4^{2-}$ is present (due to the high chloride ion concentration) resulting in the observed decrease in the extraction of platinum. This effect disappears at higher Sn:Pt ratios since more of the extractable platinum-tin species is present.

Increased chloride ion concentrations (at fixed [H^+] = 1.4M) resulted in considerably less platinum being extracted at all the Sn:Pt ratios examined, again this effect is more pronounced at low Sn:Pt ratios.

3.5 The Effect of Oxidation State of Platinum

Spectrophotometric studies have shown that the reaction between Pt(II) and Pt(IV) with tin(II) chloride in hydrochloric acid solution results in the formation of identical colours [94]. Ayres and Meyer [94] have shown that spectral curves obtained for both the platinum(IV) and platinum(II)-tin(II) systems were identical except that maxima for the platinum(IV)-tin(II) system occurred at mole fractions corresponding to one mole less of tin per mole of platinum. It was thus evident that platinum(IV) is reduced to platinum(II) which then reacts with the tin(II) chloride to form the coloured product. In this reaction one mole of tin(II) is utilized (per mole of Pt(IV)) and oxidised to tin(IV) simultaneously with the reduction of Pt(IV) to Pt(II).

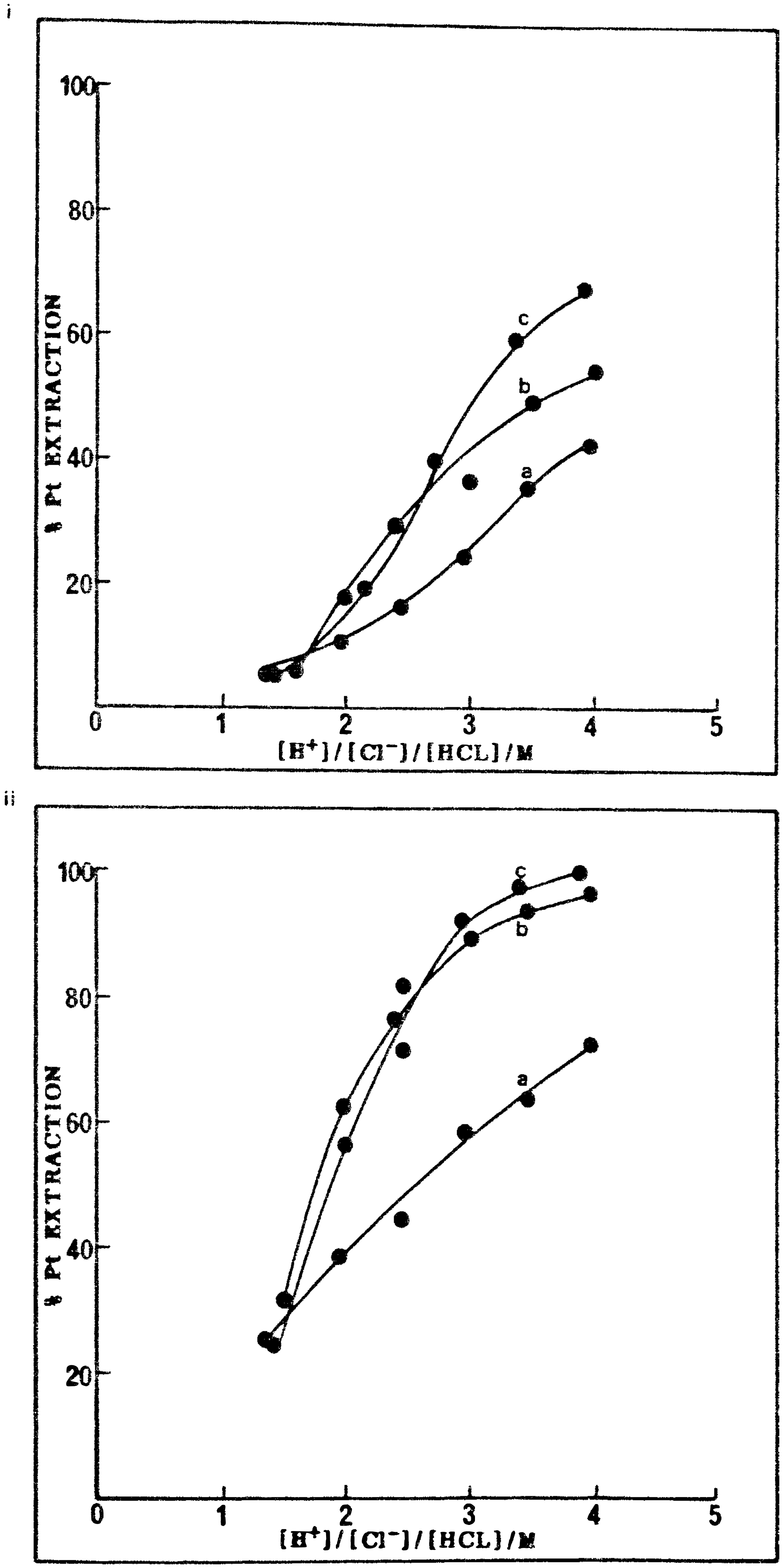


Figure 3.7 The effects of (a) $[Cl^-]$ (b) [HCL] (c) $[H^+]$ on the extraction of platinum by 40% MIBK at Sn(II):Pt(II) ratios of (i) 2 and (ii) 5

In order to gain more knowledge about the effect of the oxidation state of platinum on its extraction in our system, experiments were performed in which aqueous phases containing Pt(IV) and Sn(II) at various ratios were equilibrated and extracted into MIBK-hexane mixtures. Figure 3.8 illustrates the results of these experiments at 2.4M HCL.

It is evident that percentage extraction of platinum at a Sn(II):Pt(IV) ratio of 5:1 is less than that for the corresponding Sn(II):Pt(II) ratio. Instead results obtained agree very well with those obtained for the 4:1 Sn(II):Pt(II) ratio clearly sug-

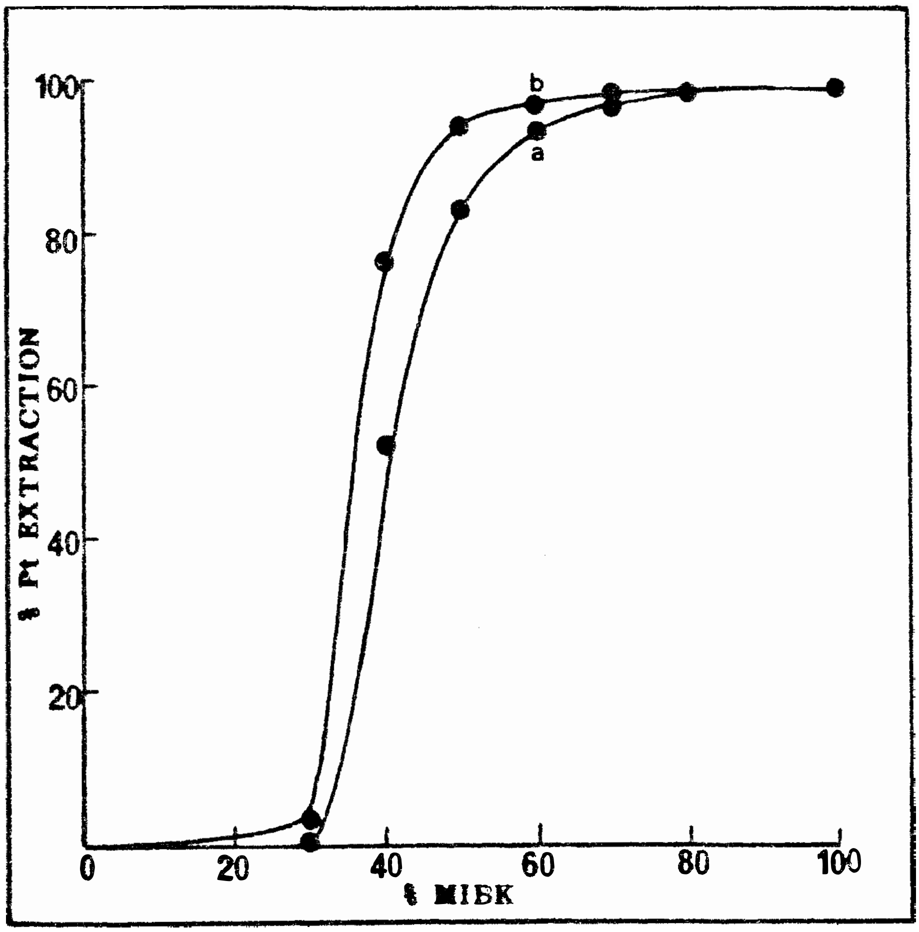


Figure 3.8 The effect of the oxidation state of platinum on its extraction from 2.4M HCL solutions at:
(a) Sn(II):Pt(IV) ratio of 5
(b) Sn(II):Pt(II) ratio of 5

gesting that reduction of Pt(IV) to Pt(II) had occurred in the presence of tin(II) chloride. It is virtually impossible to detect this effect at higher Sn(II):Pt(IV) ratios since the presence of excess tin(II) chloride results in complete extraction of platinum, irrespective of whether reduction of Pt(IV) has taken place or not.

3.6 The Effect of Equilibration Time

In Section 2.3.1 of Chapter 2 we said that sufficient time must be allowed for the formation of the Pt-Sn complex in aqueous acid solutions. Subsequent experiments by Yates [50] demonstra-

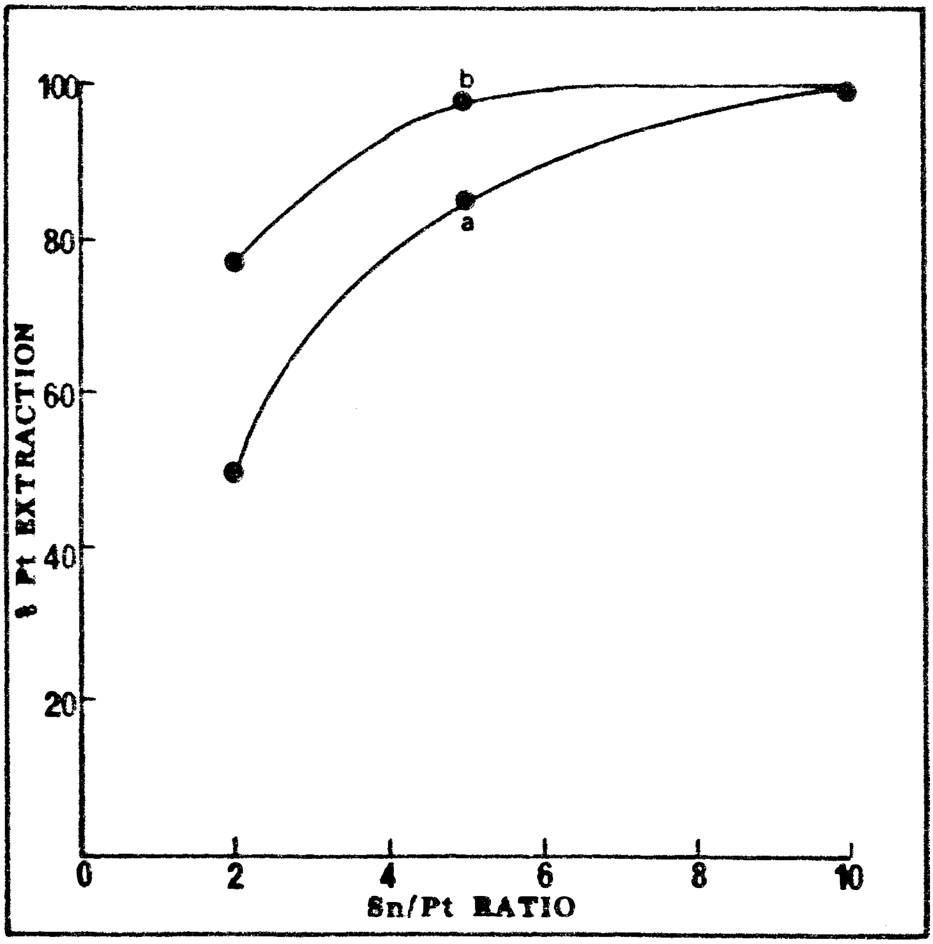


Figure 3.9 The effect of the Sn:Pt ratio on the extraction of platinum with (a) 0 minutes and (b) 20 minutes pre-equilibration of the aqueous phase.

ted that for aqueous solutions of Sn(II):Pt(II) ratio 2 at 1.5M HCL, 20 minutes was necessary for equilibrium to be reached as measured by the constancy of the absorbance spectra.

It was thus shown that at low Sn:Pt ratios the formation of the Pt-Sn complex was presumably a relatively slow process which if not taken into consideration could result in incomplete extraction of platinum. At high Sn:Pt ratios the rate of formation of the Pt-Sn complex may be expected to be more rapid due to the presence of excess $SnCl_3^-$.

Extraction experiments were performed in 1.4M HCL at various Sn:Pt ratios with and without pre-equilibration of the aqueous phase. Results shown in Figure 3.9 clearly illustrate that percentage extraction of platinum is lower at the low Sn:Pt ratios *(ca* 2 and 5) with no equilibration of the aqueous phase, an observation which may be attributed to the relatively slow process of formation of the Pt-Sn complex. However, high Sn:Pt ratios *(ca* 10) result in complete extraction of platinum irrespective of whether the aqueous phase had been pre-equilibrated or not, presumably due to the rapid formation of the Pt-Sn complex.

CHAPTER 4

CHAPTER 4

4. SOLVENT EXTRACTION OF PALLADIUM

Preliminary qualitative experiments (Chapter 2 Section 2.3.2) have shown that the rate of reaction between stannous chloride and $PdCl_4^{2-}$, and extraction of the complexes so formed into MIBK, is somewhat more rapid than for the platinum analogue. For this reason shorter extraction and equilibration times of 5 and 15 minutes respectively were employed in all experiments performed.

Strict precautions were taken to perform all the extractions under nitrogen and to exclude air at all times and variations of the experimental procedures used in the solvent extraction of platinum were kept to an absolute minimum so as to afford a comparison of the extraction behaviour of these two metals.

4.1 The Effect of Sn(II):Pd(II) ratio

Treatment of palladium(II) with tin(II) chloride showed the existence of at least 3 complex species viz., yellow, red and green depending on the experimental conditions [35]. The most stable complex of Pd(II) with tin(II) chloride in aqueous solutions is the green form which is produced slowly at low concentrations of $SnCl_2$; increase in $SnCl_2$ concentration led to more rapid complex formation.

Hydrochloric acid solutions containing ratios of Sn(II):Pd(II) ranging from 2 to 12 were equilibrated for 15 minutes followed by extraction into 100% MIBK.

Three sets of extractions were performed as described at 1.4, 2.4 and 3.4M HCL followed by analysis of the separate phases by AAS. Percentage palladium extracted was calculated by comparison with blanks for each different ratio. Prior to extraction the colours of the aqueous phases were observed to vary from light orange-green (at ratios of *ca* 2) to a very dark olive-green at high Sn:Pd ratios. Both the aqueous and organic phases showed considerable changes in colour after extraction. Aqueous phases were observed to vary from a very light-yellow to dark-green to dark-brown depending on the acid concentration whereas the organic layers varied from yellowish-orange to red at high ratios.

The extraction profiles for percentage palladium extracted under these conditions is shown in Figure 4.1.

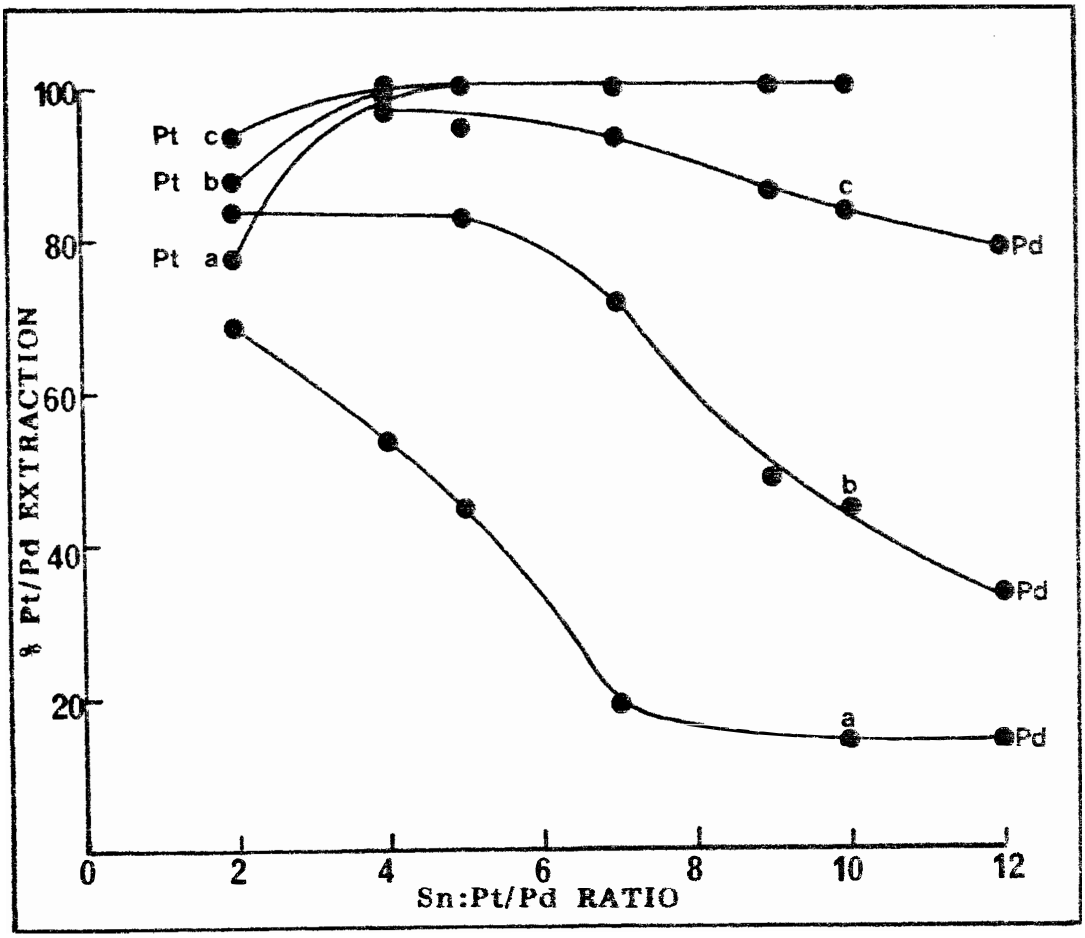


Figure 4.1 The effect of the Sn(II):M(II) ratio (M = Pd, Pt) on the extraction of Pd(II) and Pt(II) by pure MIBK from (a) 1.4M (b) 2.4M and (c) 3.4M HCL solutions

It is clearly evident that the extraction of palladium is dependant on the Sn(II):Pd(II) ratio. However it was found that the presence of increasing amounts of stannous chloride decreases the percentage palladium extracted into the organic phase. A significant difference between the extraction behaviour of palladium and platinum is thus immediately evident. At larger Sn(II):Pd(II) ratios the amount of palladium extracted is considerably reduced (especially at lower acidities) with most palladium being extracted at the low Sn(II):Pd(II) ratios. In contrast extraction of platinum under similar conditions results in complete extraction at high Sn(II):Pt(II) ratios (see Figure 4.1).

This unexpected type of behaviour naturally led to questions about the reasons for these observations. It has been reported that at a 1:2 Pd(II):Sn(II) ratio an unstable palladium hydrosol is thought to be formed [36] as a result of the reaction

$$Pd^{2} + Sn^{2+} \rightleftarrows Pd^{o} + Sn^{4+}$$

Hence in the presence of Sn^{2+}, Pd^{2+} is probably reduced to the metal, Pd^{o}.

It seems that the rate of this reaction increases with increased Sn(II) concentration, so that at a Sn(II):Pd(II) ratio of 10:1 more Pd(II) is reduced (during the equilibration and extraction times) resulting in less palladium being extracted (presumably the reduced form of palladium is not extractable). Experiments were performed at various Sn:Pd ratios in 2.4M HCL in which extraction was carried out immediately after preparation of the aqueous phase i.e, no equilibration period was allowed for the aqueous phase. This would allow little or no time for the formation of the non-extractable form of palladium and hence we expect more palladium to be extracted.

Figure 4.2 shows that an increase in extraction does occur. Similar trends were observed when the experiment was repeated in 3.4M HCL. This phenomenon was however not evident in the case of platinum so that this difference between platinum and may serve as a good basis for the separation of these two noble metals.

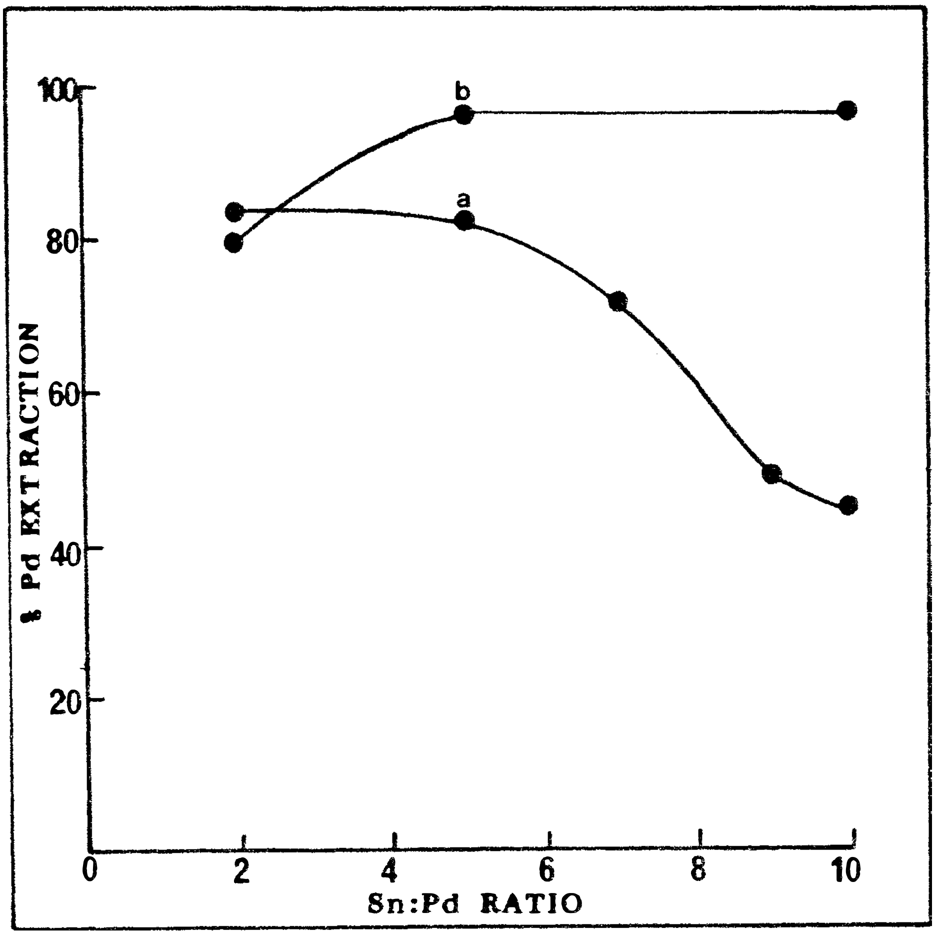


Figure 4.2 The extraction of palladium (a) with and (b) without pre-equilibration of the aqueous phase from 2.4M HCL solutions by pure MIBK as a function of initial Sn:Pd ratio

Experiments were also performed at fixed acid concentrations to determine the effect of the organic phase composition on the extraction of palladium at various Sn(II):Pd(II) ratios. Results so obtained are shown in Figure 4.3. As in the case of platinum, the amount of palladium extracted from solutions containing fixed Sn(II):Pd(II) ratios was also found to be dependant on the percentage of MIBK in the organic phase. Thus for a fixed Sn(II):Pd(II) ratio the colour intensities of the organic phase was generally observed to vary from colourless (0%

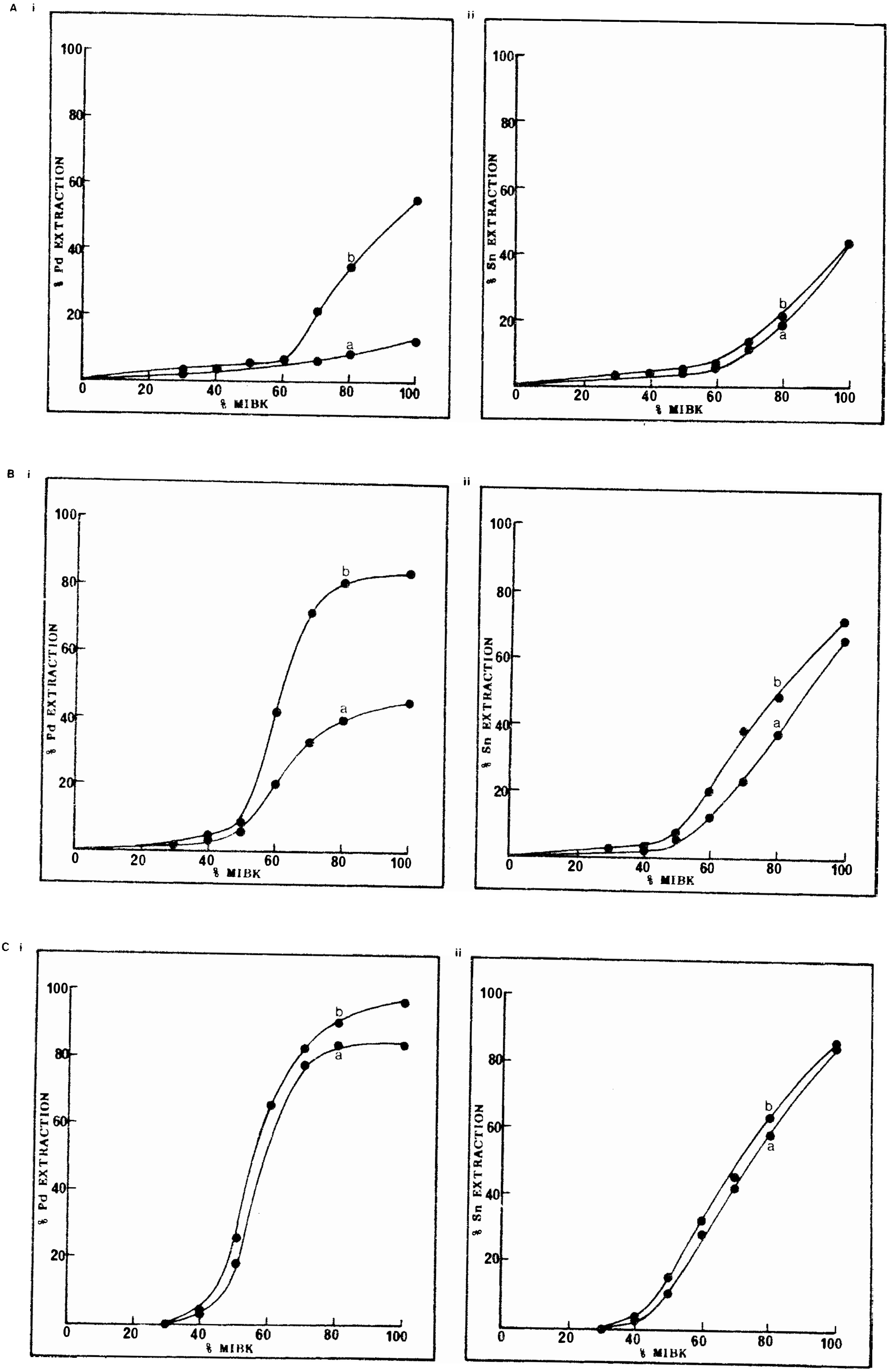


Figure 4.3 The variation of percentage extraction of (i) palladium and (ii) tin from
(A) 1.4M
(B) 2.4M
(C) 3.4M
HCL solutions with % MIBK at Sn(II):Pd(II) ratios of (a) 10 and (b) 5

MIBK) to yellow-orange (50% MIBK) to orange-red (100% MIBK) where maximum extraction occurred for all the ratios investigated. Extraction of palladium generally increases with increased percentages of MIBK.

The dependence of the distribution coefficient of palladium on the MIBK concentration in the organic phase was also determined. The results obtained are illustrated in Figure 4.4 and comparison with Figure 3.2 clearly indicates considerable differences in the extraction yields of platinum and palladium.

4.2 The Effect of Hydrochloric Acid Concentration

Ayres and Meyer [16] found previously that the amount of palladium extracted increased with a decrease in hydrochloric acid concentration. However in Figure 4.1 it was clearly shown that extraction of palladium *increases* with increased acid concentrations up to 3.4M HCL. It was thus decided to investigate the effect of HCL concentration on the extraction of palladium into various MIBK-hexane mixtures.

The extraction of palladium from HCL solutions of varying concentration containing $PdCl_4^{2-}$ and $SnCl_2$ in a predetermined molar ratio results in the extraction profiles shown in Figure 4.5. Although we performed our extractions at 3 different acid concentrations only, the results obtained clearly indicate the effect of hydrochloric acid on the extraction of palladium. An increase in the percentage palladium extracted is observed with an increase in HCL concentration for all the Sn(II):Pd(II) ratios investigated. However, this effect appears to be less pronounced at high Sn:Pd ratios (*ca* 10). The extraction of palladium increases sharply at > 50% MIBK reaching a maximum at 3.4M HCL for all the ratios investigated. At fixed HCL concentration, extraction is again observed to increase with increased percentages of MIBK.

4.3 The Effect of Hydrogen Ion Concentration

Experiments to determine the effect of hydrogen ion concentra-

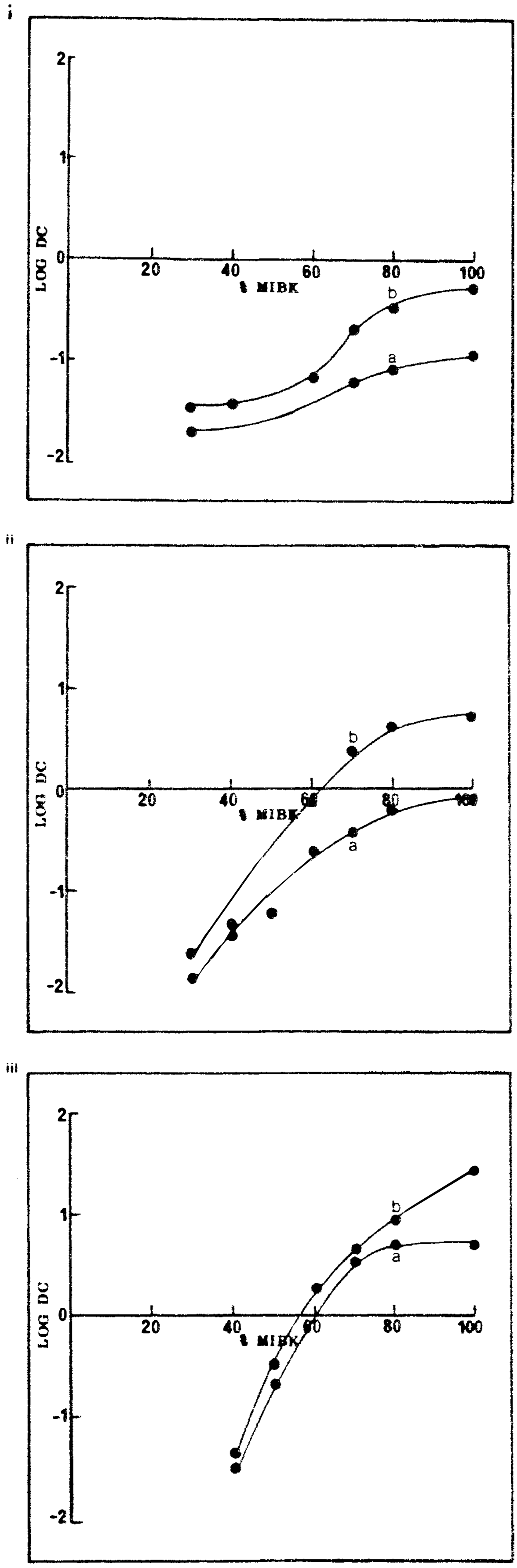


Figure 4.4 The dependence of the distribution coefficients of palladium on the concentration of MIBK in the organic phase after extraction from (i) 1.4M (ii) 2.4M and (iii) 3.4M HCL solutions at Sn(II):Pd(II) ratios of (a) 5 and (b) 10

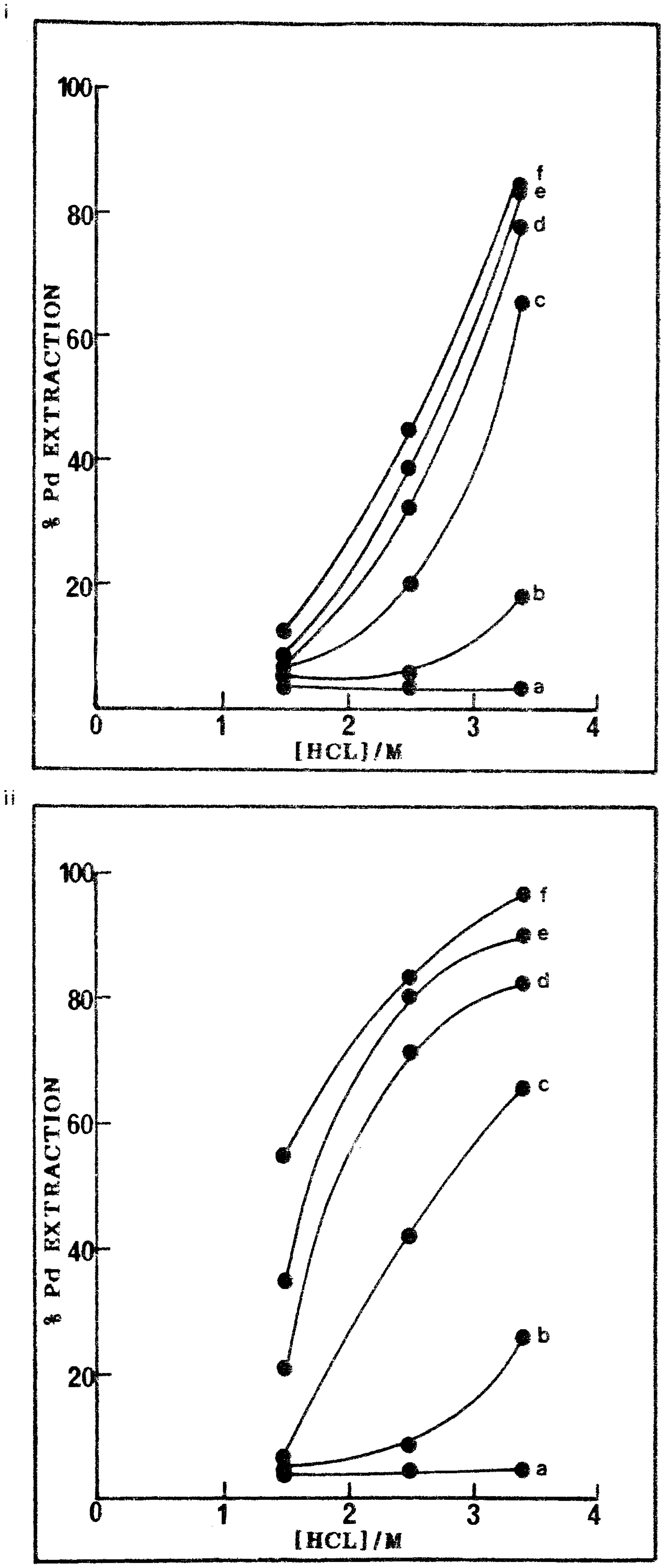


Figure 4.5 The effect of hydrochloric acid concentration on the extraction of palladium (a) 40 (b) 50 (c) 60 (d) 70 (e) 80 and (f) 100 %MIBK at Sn(II):Pd(II) ratios of (i) 5 and (ii) 10.

tion on the extraction of palladium were performed under an inert atmosphere of nitrogen utilising similar experimental procedures as for platinum. (Section 3.3 Chapter 3). Results so obtained are shown in Figure 4.6 which shows the variation of percentage palladium extracted with hydrogen ion concentration at various Sn(II):Pd(II) ratios.

Some interesting trends may be noted from these results. The percentage extraction of palladium generally increases with an increase in hydrogen ion concentration. The colours of the organic phases paralleled this trend, varying from colourless/light-yellow at low H^+ concentrations to dark orange-red at the highest H^+ concentration, at which point maximum extraction occurred. Complete extraction of palladium did not occur at any of the Sn(II):Pd(II) ratios investigated. As noted previously (Section 4.1), the extraction of palladium was found to be higher at lower ratios of Sn:Pd.

Similarity in the mechanism of extraction of platinum and palladium is thus suggested, since increased hydrogen ion concentrations resulted in increased extraction of both metals. However, the lower percentage extraction of palladium observed at high Sn(II):Pd(II) ratios could be exploited to our advantage in order to effect a separation of platinum and palladium.

4.4 The Effect of Chloride Ion Concentration

Similar extraction experiments to determine the effect of chloride ion concentration on the extraction of platinum (Section 3.4) were performed with palladium. Chloride ion concentrations chosen were from 1.4 to 4M for all the ratios investigated, with extreme care being taken to exclude air at all times during the actual extraction.

In the case of platinum, increased chloride ion concentrations resulted in an overall decrease in the percentage platinum extracted. A similar trend might be expected for palladium and Figure 4.6 (see Section 4.3) clearly illustrates that increased

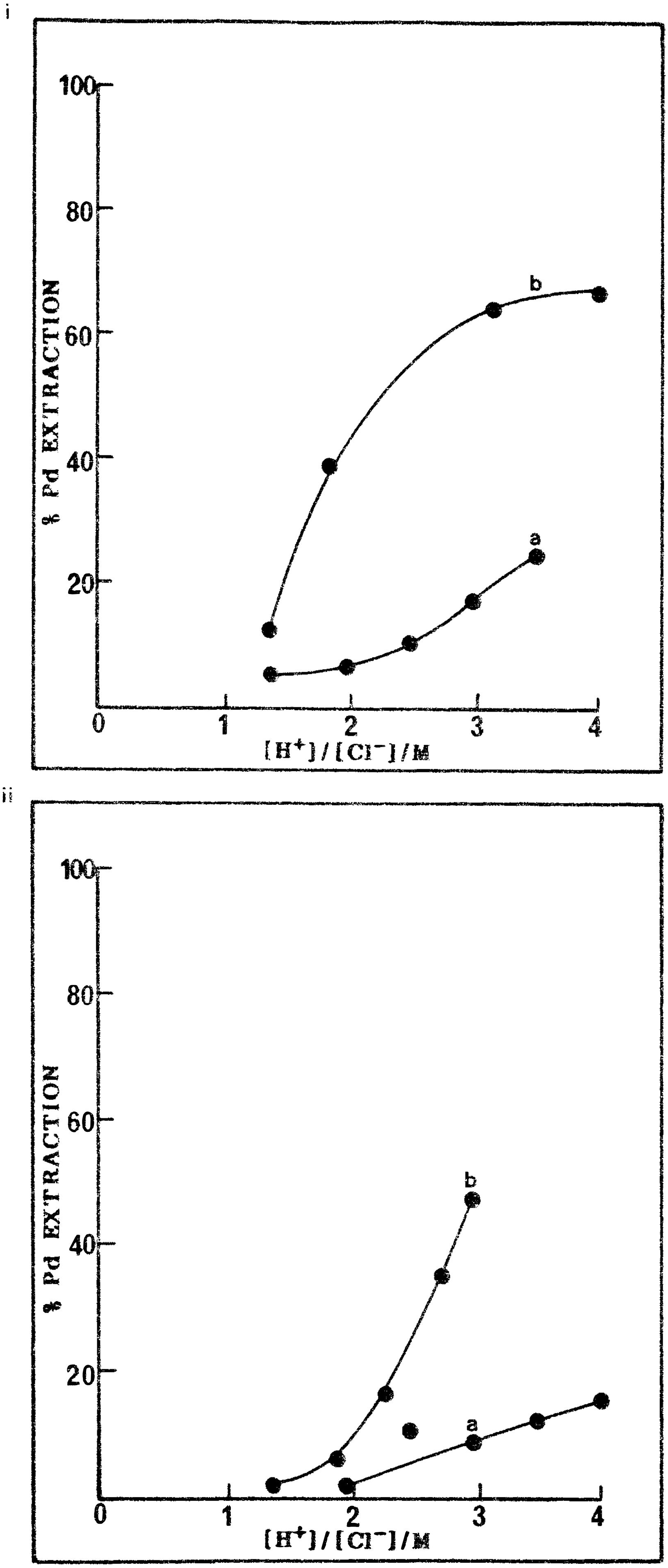


Figure 4.6 The effect of (a) chloride ion concentration (fixed $[H^+]$ = 1.4M) and (b) hydrogen ion concentration (fixed $[Cl^-]$ = 1.4M) on the extraction of palladium by 40 %MIBK at Sn(II):Pd(II) ratios of (i) 5 and (ii) 10.

chloride extraction results in a gradual increase in the extraction of palladium. However percentage extraction of palladium was considerably less when compared with that extracted over the corresponding range of H^+ and HCL concentrations. The colour of the aqueous phases before extraction was observed to vary from dark-green to orange-green as the chloride ion concentration increased, while the colour of the organic phases ranged from colourless to yellow on extraction.

4.5 The Effect of Equilibration Time

It has been shown that reduction of Pd^{2+} to Pd^o by Sn^{2+} occurs and that the rate of this reduction increases with increased Sn(II) concentration resulting in less palladium being extracted at high Sn(II):Pd(II) ratios (Section 4.1). However, when no equilibration period was allowed for the aqueous phase, a marked increase in percentage palladium extracted is observed; in fact complete extraction (100%) of palladium occurs at high Sn(II):Pd(II) ratios.

It is thus clear that the amount of palladium extracted varies not only with Sn(II):Pd(II) ratio but with the equilibration time of the aqueous phase as well. It seemed logical to assume that more reduction would occur if palladium was left longer in contact with the tin resulting in less extraction into the organic phase. Experiments were thus performed at a 10:1 Sn(II):Pd(II) ratio in 2.4M HCL in which the pre-equilibration of the palladium-tin phase was varied from 0 - 60 minutes before extraction into 100% MIBK. As in all previous experiments, percentage metal extracted was determined.

Figure 4.7 shows the variation of percentage palladium and tin extracted as a function of equilibration time. As predicted, percentage palladium extracted decreases with increased equilibration of the aqueous phase. The reduction process however appears to be relatively slow since the extraction of palladium was observed to decrease from 100% with no pre-equilibration to ≃ 20% after 60 minutes pre-equilibration of the aqueous phase.

The colours of the organic phases were observed to conform to the decrease in extraction of palladium with time, varying from red (no pre-equilibration) to orange to pale-yellow (60 minutes pre-equilibration).

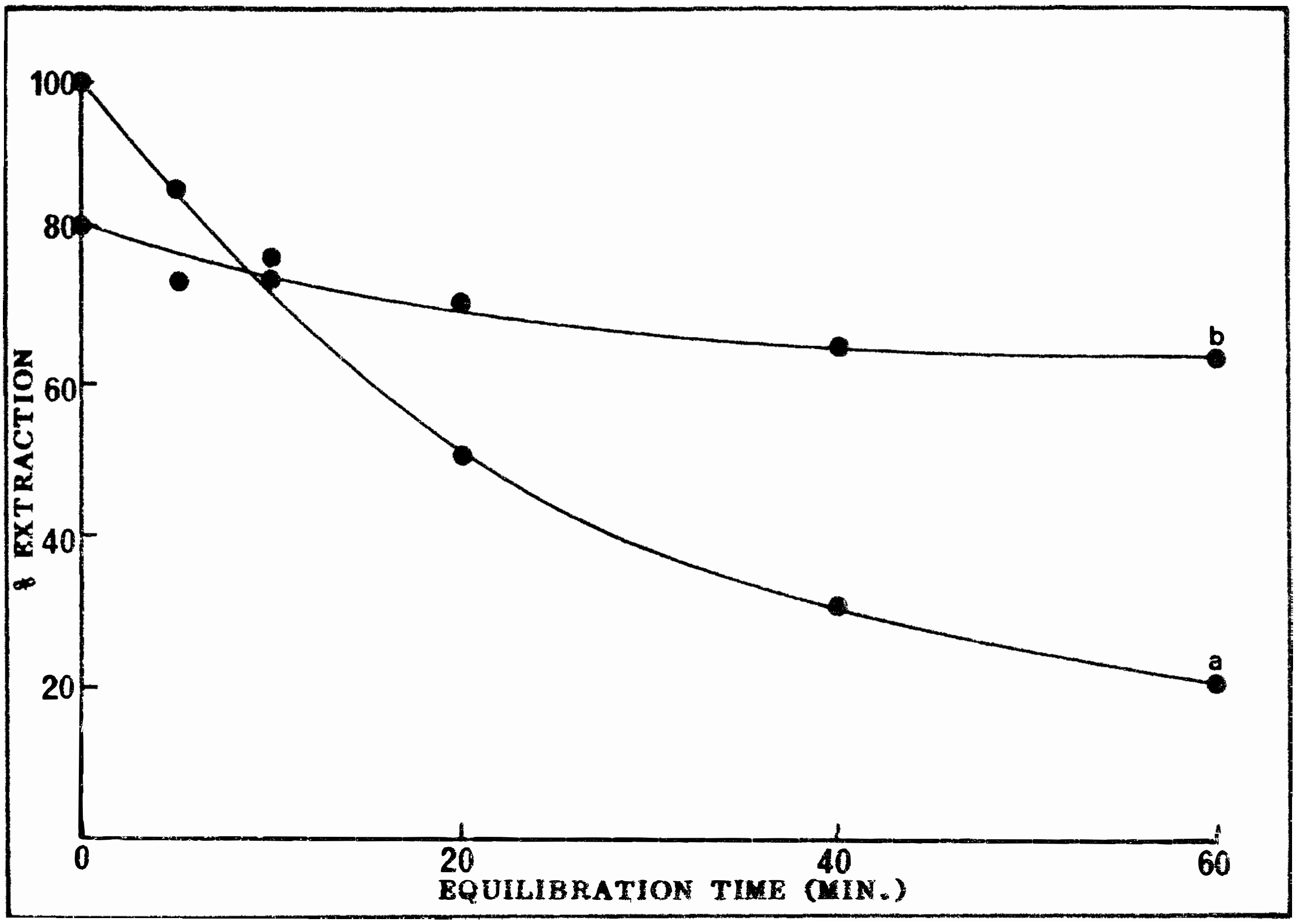


Figure 4.7 **The variation of percentage extraction of (a) palladium and (b) tin with equilibration time from 2.4M HCL solutions into pure MIBK at Sn(II):Pd(II) ratio of 10**

It may be concluded that if palladium and tin were left in contact with each other for longer periods (i.e. > 60 minutes), even less extraction should occur due to further reduction of palladium. The above observations presented us with an additional prospect of separating platinum and palladium. Apart from simply varying the amount of $SnCl_2$ present, separation of platinum and palladium could also be effected by varying the pre-equilibration time of the aqueous phase.

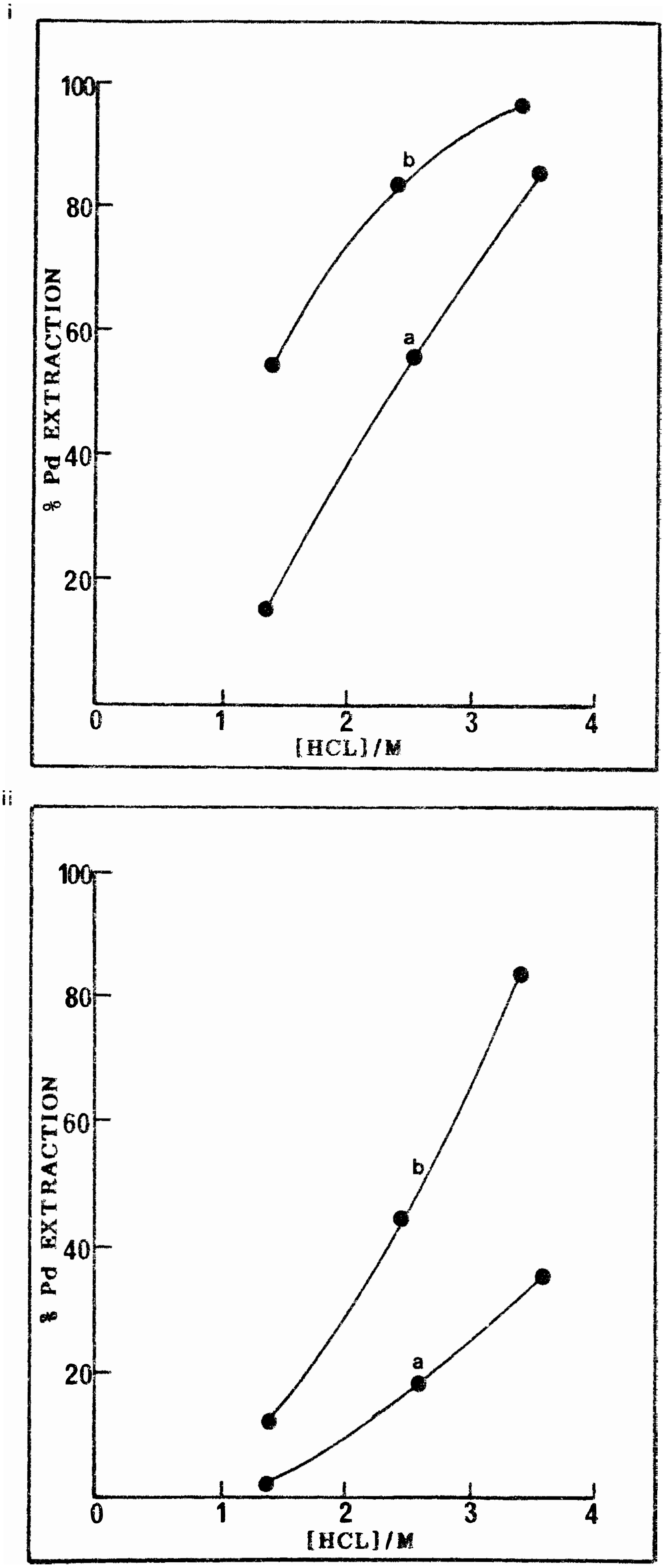


Figure 4.8 The effect of hydrochloric acid concentration on the extraction of palladium by pure MIBK at Sn(II):Pd(II) ratios of (i) 5 and (ii) 10 after (a) 20 hours and (b) 20 minutes pre-equilibration of the aqueous phase

In order to investigate the feasibility of this prospect, experiments were carried out at various acid concentrations in which the aqueous phases were pre-equilibrated for ± 20 hours under an inert atmosphere of nitrogen. A number of interesting observations regarding the aqueous phases were made prior to extraction on the following day. The colours of the aqueous phases were opaque and dark olive-green at ratios $\geq$ 5 for all the acid concentrations investigated. However at a Sn(II):Pd(II) ratio of 2, the aqueous phases varied from dark-brown to yellow-green with increased acid concentrations, and larger amounts of a black precipitate was observed in extraction tubes containing HCL concentrations greater than 1.4M. Nevertheless, we proceeded to extract the palladium from the pre-equilibrated aqueous phases into organic phases containing only pure MIBK. Figure 4.8 shows the variation of percentage palladium extracted (after 20 minutes and 20 hours pre-equilibration respectively) as a function of acid concentration. It can be seen that less palladium is extracted with longer pre-equilibration of the aqueous phase, especially at lower acid concentrations.

A small interphase precipitate was observed between the MIBK and the aqueous phases after extraction. The formation of this precipitate was however virtually absent at Sn:Pd ratios of 10, where very little or no precipitate was present.

Samples of the precipitate formed at Sn:Pd ratios of 2 and 5 were filtered off, washed thoroughly with distilled water and found to be soluble in nitric acid. Qualitative analysis by AAS revealed that the precipitate consisted mainly of palladium.

CHAPTER 5

CHAPTER 5

5. SOLVENT EXTRACTION SEPARATION OF PLATINUM AND PALLADIUM

The prospect of separating platinum and palladium by varying the pre-equilibration time could not be realised until suitable ways and means could be found for a complete elimination of the draw- backs mentioned on p 74 of Chapter 4). Since further investigations to this effect were not carried out, we proceeded to investigate the possibility of separating platinum and palladium by simply varying the amount of $SnCl_2$ present.

A complete survey of all our experimental data concerning the extraction of platinum and palladium thusfar, revealed that the separation of these two noble metals (by varying the amount of $SnCl_2$ present) could best be achieved under the following conditions:

	SEPARATION CONDITIONS						
	1	2	3	4	5	6	7
HCL Conc. (M)	1.5	1.5	1.5	2.5	2.5	3.5	3.5
Pt/Pd : Sn ratio	1:5	1:10	1:10	1:5	1:10	1:5	1:10
% MIBK	60	60	60	50	50	40	40
Equilibration Time (min.)	20	20	60	20	20	20	20
Extraction Time (min.)	10	10	10	10	10	10	10
% Pt extraction expected	±88	±100	±100	±95	±97	±94	±99
% Pd extraction expected	±7	±6	?	±8	±6	±4	±3

Table 5:1 Optimum experimental conditions predicted for the separation of platinum and palladium

The equilibration time in (3) was considered to be too time-consuming and hence a separation under these conditions was not attempted. Extraction and equilibration times chosen for the remaining conditions of separation were analagous to those used in the solvent extraction of platinum. However figures quoted for "percentage palladium extraction expected" under separation conditions 1,2 and 4-7 were obtained using 15 minutes pre-equilibration and 5 minutes extraction and can therefore be expected to be lower during the actual separation due to the longer pre-equilibration time that is employed (viz 20 minutes).

In order to test the predictions, separation of platinum and palladium was performed over the entire range of MIBK (from 0 to 100%). It is also evident that the separation is possible at different acid concentrations.

5.1 The Effect of Hydrochloric Acid Concentration

Three sets of separations were performed at 1.4, 2.4 and 3.4M HCL with appropriate tin(II) and platinum(II)/palladium(II) concentrations chosen for the various ratios. Figure 5.1 shows the results of these experiments at the different acid concentrations.

Evidently, optimum separation of platinum and palladium is achieved under previously predicted conditions. Complete separation occurred at 60% MIBK in 1.4M HCL for a Sn:Pt/Pd ratio of 10 (see Figure 5.1) and sharp, clean phase separations were observed in all cases. The extraction behaviour of platinum in the presence of palladium was found to be analagous to its behaviour in the absence of palladium, but percentage palladium extraction under similar conditions was however found to be lower than usual. This is presumably due to

(1) increased reduction of palladium during the longer pre-equilibration stage of the extraction, as well as

(2) the competing effect between the anionic Pt-Sn and Pd-Sn complexes for cationic 'oxonium sites' in the organic phase.

Incomplete separation of Pt and Pd generally occurs at > 60% MIBK due to increased extraction of palladium especially at the higher acidities. This effect is even more pronounced at lower

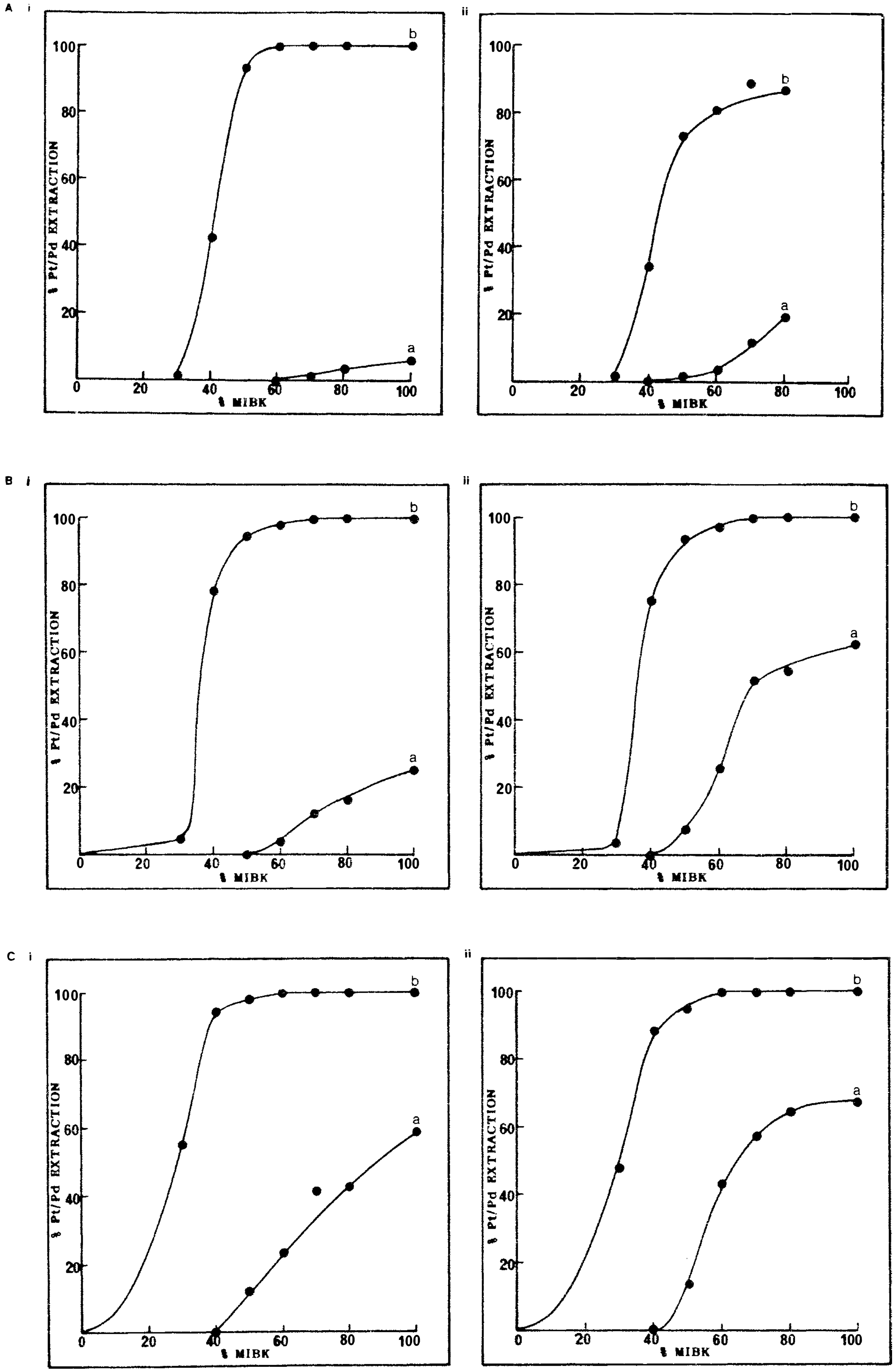


Figure 5.1 The variation of percentage extraction of (a) palladium and (b) platinum from
(A) 1.4M
(B) 2.4M
(C) 3.4M
HCL solutions with % MIBK at Sn(II):Pd(II)/Pt(II) ratios of (i) 10 and (ii) 5

Sn:Pd ratios. Maximum extraction but worst separation of Pt and Pd occurred at 100% MIBK for all the ratios and acid concentrations investigated. The formation of interphase precipitates between MIBK and the aqueous phase was not apparent in any of the separations performed.

Figure 5.2 shows the dependence of the distribution coefficients of platinum and palladium on the MIBK concentration in the organic phase at various acid concentrations. The possibility of extractive-separation of these two noble metals can be evaluated on the basis of their distribution coefficients obtained under similar conditions. High distribution coefficients were obtained for platinum in the 40-60% MIBK concentration range.

5.2 The Effect of Macroamounts of Palladium

Separation of minute amounts of a platinum element from macroamounts of another element of this group can present serious difficulties. Because of the similar chemical properties of the platinum metals only a few micro-macro separation methods have been developed [37, 38, 95], with studies being mainly concentrated on the extractive separation of similar amounts of this group of elements. In his studies Mojski *et al* [96] found that the extraction of platinum with triphenylphosphine oxide (TPPO) from solutions containing platinum and palladium unfavourably decreases with increasing palladium concentration.

Separation experiments were performed at various Pd:Pt ratios of up to 10:1 in 1.4M HCL into MIBK-hexane mixtures ranging from 50 to 100%. Appropriate amounts of tin were added to give the desired Pt:Sn and Pd:Sn ratios. All the necessary precautionary measures were taken as for the other extraction experiments and percentage platinum and palladium extracted was determined by AAS and comparison with a blank.

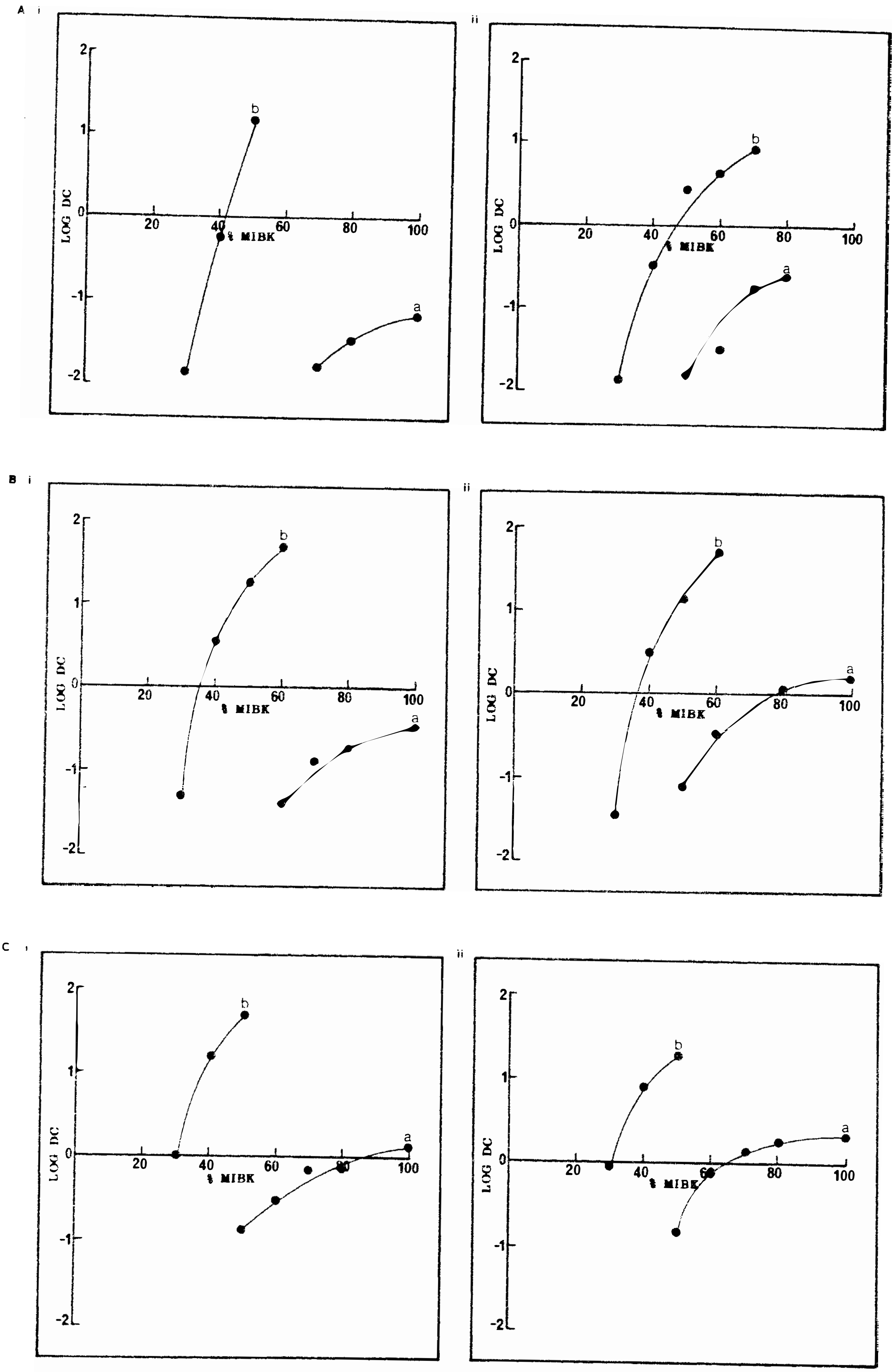


Figure 5.2 The dependence of the distribution coefficients of (a) palladium and (b) platinum on the concentration of MIBK in the organic phase after extraction from
(A) 1.4M
(B) 2.4M
(C) 3.4M
HCL solutions at Sn(II):Pd(II)/Pt(II) ratios of (i) 10 and (ii) 5

Figure 5.3 shows the results obtained under the above-mentioned conditions. It is evident that Pd:Pt ratios of up to 10 seem to have no effect on the separation process. Virtually complete separation of platinum and palladium is observed at 60% MIBK for all the Pd:Pt ratios investigated. At higher percentages of MIBK some palladium (< 10%) was co-extracted with the platinum.

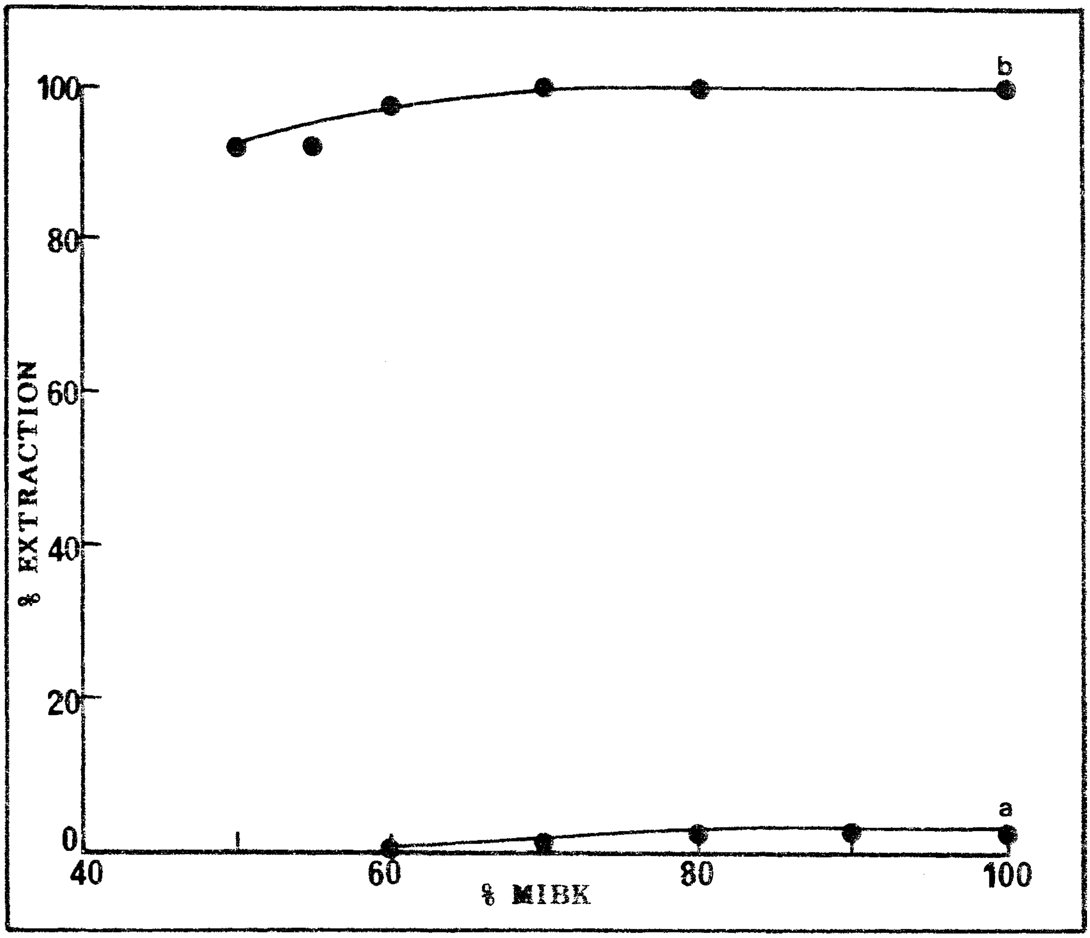


Figure 5.3 **The effect of macroamounts of palladium on the percentage extraction of (a) palladium and (b) platinum from 1.4M HCL solutions by MIBK-hexane mixtures at Sn(II):Pd(II)/Pt(II) ratio of 10**

Hence, at a platinum concentration of 228 μg/ml, amounts of palladium up to 1241 μg/ml can be tolerated without significantly affecting the separation. Higher Pd:Pt ratios were not examined.

Figure 5.4 shows that excess tin (25 fold) results in an even better separation of platinum and palladium. Complete separation is observed in the 70-100% MIBK range in 1.4M HCL at a Pt/Pd:Sn ratio of 25. Further increase in tin(II) chloride concentration could therefore be expected to result in a cleaner separation over a wider range of MIBK-hexane mixtures.

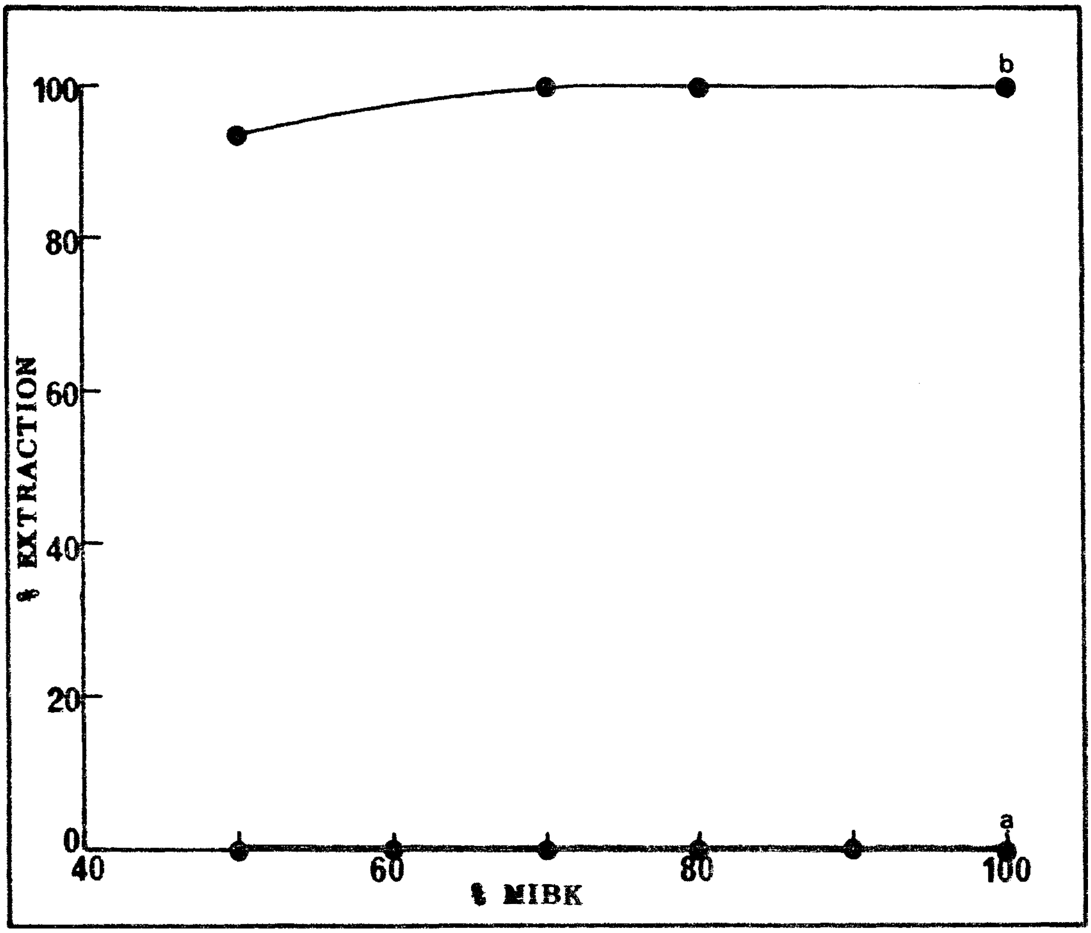


Figure 5.4 The effect of excess tin on the percentage extraction of (a) palladium and (b) platinum from 1.4M HCL solutions by MIBK-hexane mixtures at Sn(II):Pd(II)/Pt(II) ratio of 25

5.3 Preliminary Interference Study

The platinum group metals occur in minute quantities in deposits of copper-nickel sulphide ore. The ore concentrate produced by mineralurgical and fire-metallurgical methods consists of about 50% platinum group metals, the remainder of gold, copper, nickel and other base metals viz., iron, cobalt etc. Since these base metals are most likely to be present in solutions obtained from real samples, it is important to determine which of these elements interfere with the separation and how the interference may be overcome.

Four base metals most commonly associated with platinum (viz., Co, Cu, Fe and Ni) were tested to ascertain their effect on the separation process. Studies of the distribution of metal ions between HCL and pure MIBK by Boswell and Brooks [97] revealed that only copper (in the absence of Pt, Pd and Sn) could be expected to coextract to some extent (±5%) at HCL concentrations greater than 4M; negligible extraction of the other base metals was expected.

The small volume of analysis solution (10ml) did not permit us to investigate the effect of all the base metals on the separation at once, but two at a time. The desired amounts of base metal as nitrate were added to the aqueous phases such that the noble:base metal ratio was 1. Since Sn(II) is expected to oxidise to Sn(IV) in the presence of Fe(III)

$$2Fe^{3+} + Sn^{2+} \rightleftarrows 2Fe^{2+} + Sn^{4+}$$

it was necessary to adjust the amount of tin(II) chloride added so that the desired Pd:Sn and Pt:Sn ratios could be realised.

Figure 5.5 shows the variation of percentage extraction of platinum and palladium in the presence and absence of the base metals investigated in 1.4M HCL at Pt/Pd:Sn ratios of 1:10. It is apparent that equimolar amounts of all the base metals examined do not appear to affect the extractive separation of platinum and palladium. Percentage extraction of the base metal elements as a function of %MIBK is illustrated in Figure 5.6. Only small quantities of copper were observed to coextract with the noble metals into the organic phase; the other base metals did not extract. For the purposes of this study we did not investigate methods of circumventing the interference by copper. This interference may possibly be eliminated by devising a suitable

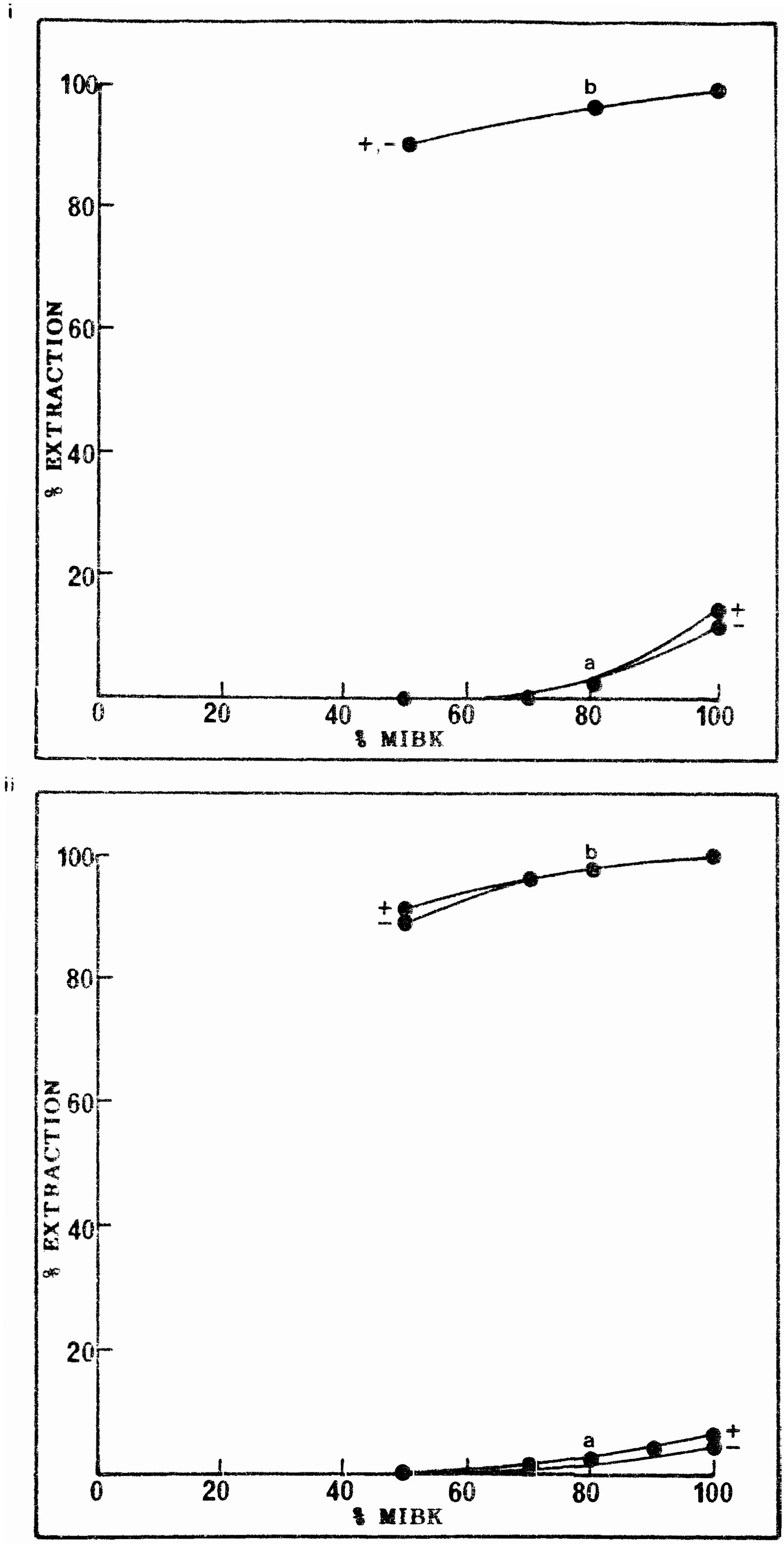


Figure 5.5 The effect of (i) Fe, Co and (ii) Ni, Cu on the percentage extraction of (a) palladium and (b) platinum from 1.4M HCL solutions by MIBK-hexane mixtures at Sn(II): Pd(II)/Pt(II) ratio of 10

backwashing procedure or by selectively complexing the copper with organic reagents provided that the noble metals are not affected.

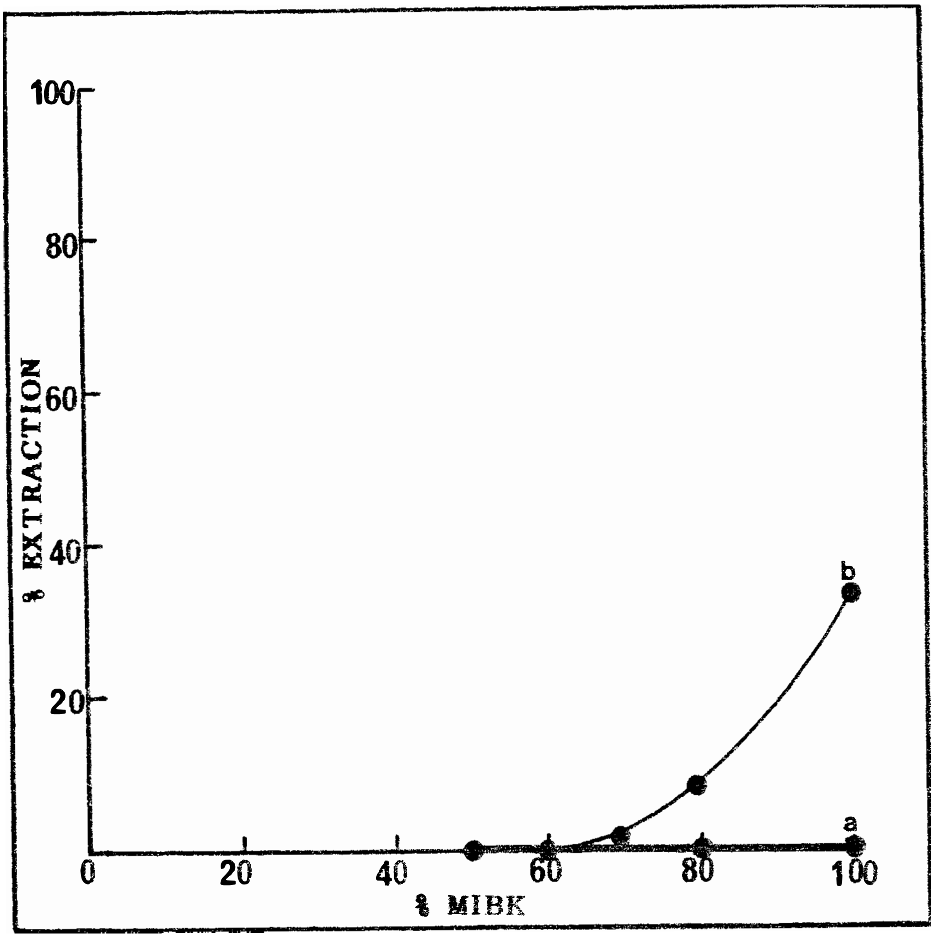


Figure 5.6 The extraction of (a) Co, Fe and Ni and (b) Cu from 1.4M HCL solutions by MIBK-hexane mixtures at Sn(II):Pd(II)/Pt(II) ratios of 10.

CHAPTER 6

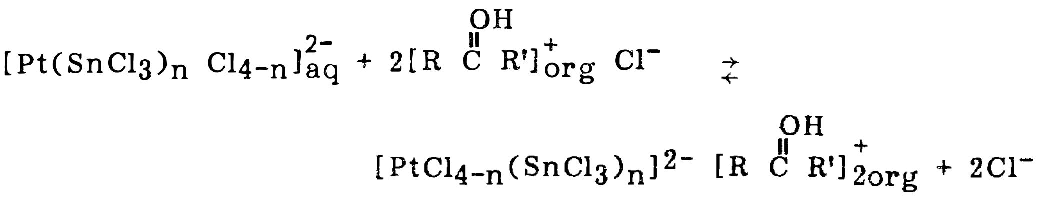
CHAPTER 6

6. DISCUSSION AND CONCLUSIONS

Results obtained from our studies on the extraction of platinum and palladium from stannous chloride solutions into MIBK-hexane mixtures have provided useful information regarding the mechanism of extraction involved in such processes, as well as the possibility of separating these two noble metals. The extraction was found to be quite complicated and affected by a number of factors. However, on the basis of our final results we were able to propose a reasonable mechanism for the extraction process and develop a feasible scheme for the separation of platinum and palladium.

The presence of varying amounts of stannous chloride dramatically affected the percentage platinum extracted. Increased amounts of stannous chloride increases the extraction of platinum from HCL solutions into MIBK-hexane mixtures. It is thought that the mechanism for the process of extraction of platinum from stannous chloride solutions involves the association of possible anionic platinum-tin complexes with a protonated, cationic MIBK species resulting in the formation of a neutral extractable species (i.e. an ion-association complex) which is soluble in MIBK-hexane mixtures.

The variation of percentage platinum extraction with HCL concentration confirmed that the primary mechanism of extraction appears to be an ion-pair formation between anionic platinum-tin chloride complexes of the form $[PtCl_{4-n}(SnCl_3)_n]^{2-}$ (n = 1 to 4) and $[Pt(SnCl_3)_5]^{3-}$ and solvated protons (oxonium ions) in the form $[MIBK\text{-}H]^+$ according to the equation:



$$[Pt(SnCl_3)_n\ Cl_{4-n}]^{2-}_{aq} + 2[R\ \overset{\overset{OH}{\|}}{C}\ R']^{+}_{org}\ Cl^- \rightleftarrows [PtCl_{4-n}(SnCl_3)_n]^{2-}\ [R\ \overset{\overset{OH}{\|}}{C}\ R']^{+}_{2org} + 2Cl^-$$

In general therefore as the concentration of HCL in the aqueous phase increases, so does the concentration of the oxonium ions in the organic phase and hence the amount of platinum extracted correspondingly increases. Additional experiments carried out to determine the effect of the organic phase composition on the extraction provided further evidence in support of our proposed mechanism (see Figure 3.4). The gradual increase observed in the extraction of the platinum as percentage MIBK increases may be attributed to the presence of ever increasing concentrations of oxonium ions resulting in increased extraction.

Increased concentrations of hydrogen ion in the aqueous phase (at fixed Cl^- concentration) also increases the concentration of oxonium ions in the organic phase thereby resulting in the observed increase in the extraction of platinum.

A possible explanation for the observed effect of increased chloride concentration (at fixed H^+ concentration) on the extraction may be proposed. It is known that a number of species are formed when stannous chloride is prepared in HCL medium. Figure 6.1 shows the distribution of tin(II) chloride complexes as a function of chloride concentration. Two of these species which are likely to be formed in equilibrium with each other are:

$$SnCl_4^{2-} \rightleftarrows SnCl_3^- + Cl^-$$

At high chloride concentration the above equilibrium would be shifted to the left favouring the formation of the $SnCl_4^{2-}$ species which is not known to form complexes with $PtCl_4^{2-}$/ $PtCl_6^{2-}$. The concentration of extractable platinum-tin complexes formed at high chloride concentration therefore decreases resulting in less platinum being extracted.

An increase in chloride concentration is also expected to shift the equilibria in the following equations to the left:

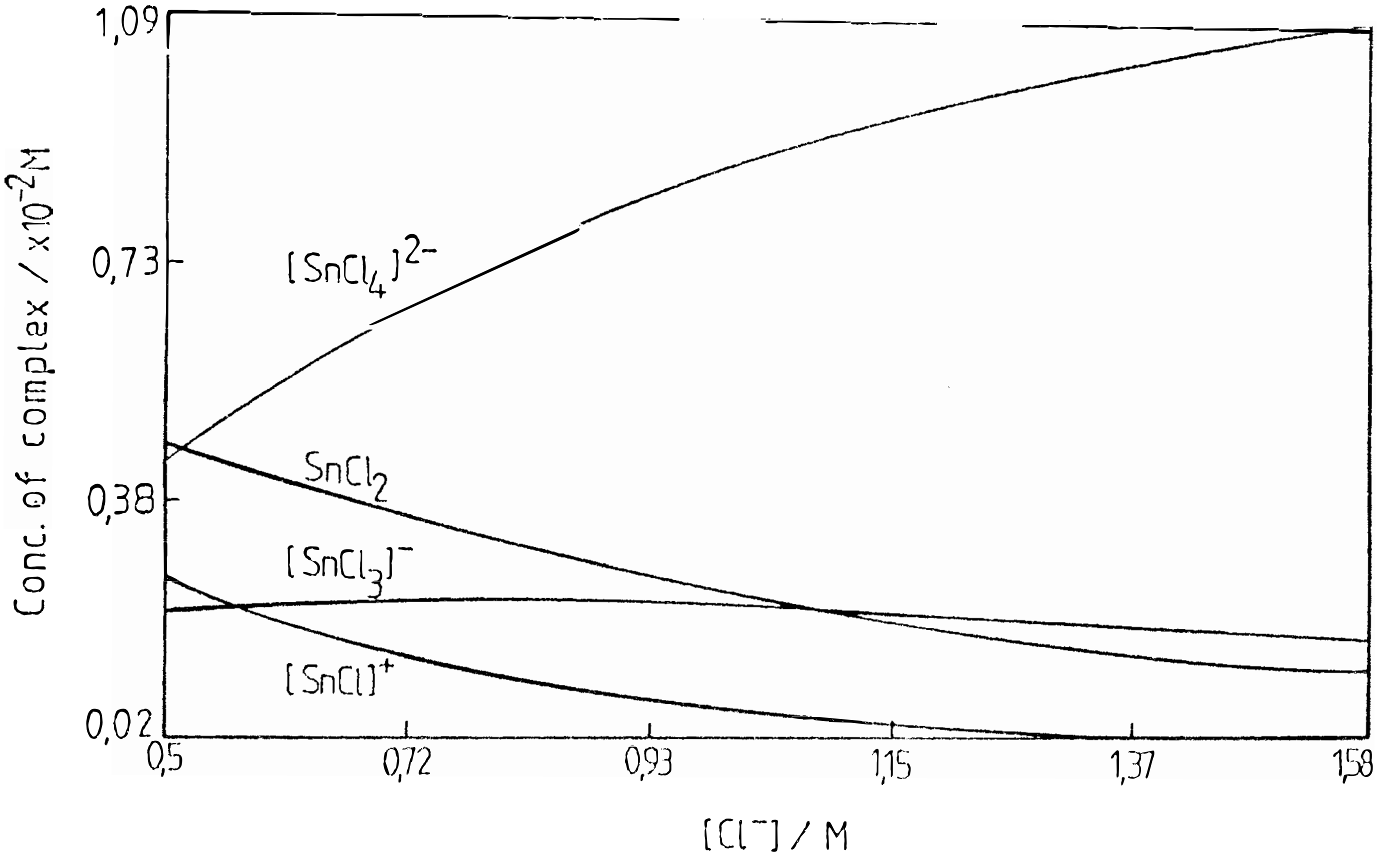


Figure 6.1 The distribution of tin(II) chloride complexes as a function of chloride concentration

(a) $[PtCl_{4-n}(SnCl_3)_n]^{2-} + 2\ [MIBK\text{-}H]^+\ Cl^-_{org} \rightleftarrows$

$[[MIBK\text{-}H^+]_2\ [PtCl_{4-n}(SnCl_3)_n]^{2-}]_{org} + 2Cl^-_{aq}$

(b) $PtCl_4^{2-} + nSnCl_3^- \rightleftarrows PtCl_{4-n}\ (SnCl_3)_n^{2-} + nCl^-$ (n=1 to 4)

Less extractable Pt:Sn complexes would therefore be formed implying that less platinum would be extracted. This has been demonstrated experimentally lending support to the mechanism postulated.

Studies on the effect of the oxidation state of platinum revealed that platinum exists in the bivalent oxidation state in the extracted anionic platinum-tin complex as suggested by an overwhelming body of evidence. It is evident therefore that extraction of the platinum-tin complex into the organic phase would only proceed if the platinum is in the 2^+ oxidation state.

The study of the effect of increasing tin(II) chloride concentration on the extraction of platinum enabled us to rationalise the observed stoichiometry of the extracted platinum-tin chloride complexes. Analysis of the aqueous phases after extraction for platinum and tin enabled us to determine by difference the corresponding molar amounts of platinum and tin present in the organic phase. The observed molar ratio of Sn:Pt in the organic phase (R_{obs}) could thus be determined.

The amount of tin extracted into the organic phase consists of tin associated with the platinum as well as tin which is independently extracted. Based on this assumption, the molar ratio of Sn:Pt in the organic phase can also be calculated theoretically (R_{calc}). Suppose we assume that platinum prefers to be extracted in the form of the $[Pt(SnCl_3)_5]^{3-}$ ion from Sn(II):Pt(II) aqueous phase ratios of ≥ 5. In this case the total amount of tin extracted into the organic phase was calculated as follows:

(i) 5 moles of tin co-extracted with each mole of platinum (based on our assumption) plus

(ii) some non-platinum associated tin that is independently co-extracted (from experimental data given in Section 2.2 Chapter 2).

The theoretically calculated ratio of Sn:Pt in the organic phase (R_{calc}) could therefore be determined.

Values calculated for R_{obs} and R_{calc} in the organic phase were then compared for extraction systems containing Sn(II):Pt(II) aqueous phase ratio ≥ 5 at various acid concentrations (see tables below). The relatively good agreement between R_{obs} and R_{calc} supports the hypothesis that platinum prefers to be extracted in the form of the $[Pt(SnCl_3)_5]^{3-}$ ion.

Pt:Sn 1:10 in aqueous phase

(a) 1.4M HCL

% MIBK	R_{obs}	R_{calc}
40	5.88	5.05
50	5.37	5.02
60	5.47	5.04
70	5.80	5.11
80	6.46	5.34
100	8.01	6.65

(b) 2.4M HCL

% MIBK	R_{obs}	R_{calc}
30	1.85	-
50	4.95	-
60	5.13	5.02
70	5.75	5.13
80	6.77	5.60
100	8.95	7.85

(c) 3.4M HCL

% MIBK	R_{obs}	R_{calc}
30	7.62	5.49
50	5.23	5.03
60	5.27	5.05
70	6.24	5.45
80	7.10	6.11
100	9.65	9.08

Pt:Sn 1:5 in aqueous phase

(a) 1.4M HCL

% MIBK	R_{obs}	R_{calc}*
40	4.69	4.03
50	4.84	4.05
60	4.67	4.05
70	4.47	4.06
80	4.55	4.13
100	4.59	4.32

(b) 2.4M HCL

% MIBK	R_{obs}	R_{calc}
30	5.79	5.01
50	4.89	-
60	5.05	5.01
70	5.08	5.01
80	5.08	5.03
100	5.47	5.34

*Assumed that 1:4 Pt:Sn complex extracted.

At lower Sn(II):Pt(II) aqueous phase ratios (*ca* < 5) platinum appears to be extractable in complexes in which not all the Cl^- ligands have been replaced by $SnCl_3^-$ ligands. The calculated and observed Sn(II):Pt(II) ratios in the organic phase appear to conform to the Sn(II):Pt(II) ratio in the aqueous phase before extraction (see tables below).

Pt:Sn 1:4 in aqueous phase

(a) 1.4M HCL

% MIBK	R_{obs}	R_{calc}*
40	2.73	-
50	4.07	3.07
60	3.73	3.06
70	3.51	3.07
80	3.54	3.13
100	3.67	3.37

(b) 2.4M HCL

% MIBK	R_{obs}	R_{calc}
30	4.00	-
50	4.37	4.01
60	4.07	4.01
70	4.01	4.00
80	3.94	-
100	4.11	4.08

(c) 3.4M HCL

% MIBK	R_{obs}	R_{calc}*
30	5.57	3.48
50	3.90	3.11
60	3.65	3.12
70	3.52	3.19
80	3.69	3.37
100	4.02	3.90

*Assumed that 1:3 Pt:Sn complex extracted

Pt:Sn 1:2 in aqueous phase

(a) 2.4M HCL

% MIBK	R_{obs}	R_{calc}
30	-	-
50	2.74	2.03
60	2.32	2.05
70	2.19	2.03
80	2.27	2.09
100	2.52	2.37

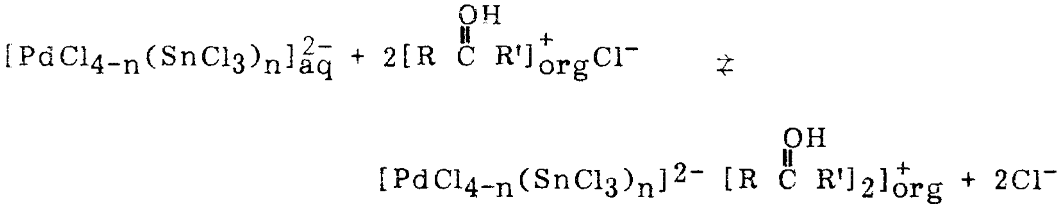
(b) 3.4M HCL

% MIBK	R_{obs}	R_{calc}
30	3.00	2.19
50	2.45	2.05
60	2.08	2.02
70	1.94	-
80	2.03	2.02
100	2.36	2.32

It is likely that a variety of platinum-tin complexes exist in solution, but in aqueous phases containing Sn(II):Pt(II) ratio 5, the pentakis(trichlorostannato)platinum(II) anion probably predominates. It is interesting to note that Young and his co-workers [13] found that solutions containing Sn:Pt ratios greater than 2:1 led to the existence of the proposed stable $[\mathrm{Pt(SnCl_3)_5}]^{3-}$ ion. In fact, a very recent multinuclear NMR study of the supposed red isomer of $[\mathrm{PtCl_2(SnCl_3)_2}]^{2-}$ isolated from 3M HCL showed it to be a mixture of the predominating red $[\mathrm{Pt(SnCl_3)_5}]^{3-}$ species and the yellow $[\mathrm{PtCl_2(SnCl_3)_2}]^{2-}$[98].

Values of R_{obs} and R_{calc} obtained by us for Sn(II):Pt(II) aqueous phase ratios of less than 5 implies that species with less than 5 $\mathrm{SnCl_3^-}$ ligands may also be extracted.

Percentage extraction of palladium was also found to be dependant on the Sn(II):Pd(II) ratio in the aqueous phase but the presence of increased amounts of $\mathrm{SnCl_2}$ decreased the percentage palladium extracted into the organic phase. Although a significant difference exists between the extractability of platinum and palladium with regard to the effect of the Sn(II):M(II) ratio, their basic mechanism of extraction appears to be comparable, at least as far as the effect of HCL concentration is concerned. If the mode of extraction for palladium is considered to be similar to that of platinum viz.



$$[\mathrm{PdCl}_{4-n}(\mathrm{SnCl}_3)_n]^{2-}_{aq} + 2[\mathrm{R}\,\overset{\mathrm{OH}}{\overset{\|}{\mathrm{C}}}\,\mathrm{R'}]^{+}_{org}\mathrm{Cl}^- \rightleftarrows [\mathrm{PdCl}_{4-n}(\mathrm{SnCl}_3)_n]^{2-}\,[\mathrm{R}\,\overset{\mathrm{OH}}{\overset{\|}{\mathrm{C}}}\,\mathrm{R'}]_2]^{+}_{org} + 2\mathrm{Cl}^-$$

then an increase in the HCL concentration of the aqueous phase should result in an increase in the concentration of oxonium ions in the organic phase thereby shifting the above equilibrium over to the right and favouring the formation of extractable ion-pairs. An increase in percentage palladium extraction with increased HCL concentration was observed (see Section 3.2).

The effect of hydrogen ion concentration on the extraction of palladium may, as in the case of platinum, be attributed to the presence of high concentrations of oxonium ions in the organic phase resulting in the observed increase in the extraction of palladium.

Similar reasons cited for the observed effect of chloride ion concentration on platinum may also be cited for palladium. In addition the replacement of the chloride ligand in the co-ordination sphere of palladium by $SnCl_3^-$ may be inhibited by high concentrations of chloride ion, resulting in the formation of less of the extractable complex species $[PdCl_{4-n}(SnCl_3)_n]^{2-}$. A decrease in the intensity of the green colour of the aqueous phase was thus observed with increased chloride ion concentration.

Having perhaps a much more significant effect on the extraction behaviour of palladium is

(1) the reduction of Pd^{2+} to Pd^o by tin(II) chloride and

(2) the effect of time on the extraction of palladium into the organic phase.

The rate of reduction increased with increased tin(II) concentration resulting in less palladium being extracted. However percentage extraction of palladium not only varies with the Sn(II):Pd(II) ratio but with the equilibration time of the aqueous phase as well. Longer equilibration of the aqueous phase resulted in less palladium being extracted. This time dependence of the extraction of palladium is probably due to two competing reactions occurring in the aqueous phase:

(a) reduction

(b) complexation

With prolonged equilibration of the aqueous phase, reduction of palladium increases resulting in less palladium being extracted. Considerably shorter equilibration times result in almost quantitative extraction of palladium since no significant reduction had occurred at this stage. This indicates that the reduction process is kinetically slower than the complexation reaction.

The prospect of separating platinum and palladium by simply varying the amount of $SnCl_2$ present was easily realised.

Results obtained showed that the separation was dependent on the HCL concentration of the aqueous phase as well as the composition of the organic phase. Complete separation of platinum and palladium can be attained in 1.4M HCL at 60% MIBK for Sn:Pt/Pd ratios of 10. The advantage of this method is that separation of these two noble metals can be achieved by a process involving only one step.

Macroamounts (up to 10 times as much) of palladium had no effect on the separation process and a large excess of tin (25 fold) resulted in an even better separation over a wider range of MIBK-hexane mixtures.

A preliminary study of the effect of four base metals on the separation revealed that only small amounts of copper coextract with the noble metals into the organic phase. However, copper as well as the other three base metals viz Fe, Co and Ni had no affect on the percentage extraction during the separation of the 2 noble metals in question.

Conclusion

We have confirmed that the presence of increased amounts of stannous chloride dramatically increases the extraction of platinum from aqueous HCL solutions of K_2PtCl_4 into hexane containing various amounts of MIBK. In contrast however, percentage extraction of palladium decreases under similar conditions. Results showed that both the amount of platinum and palladium extracted was dependant on the Sn(II):M(II) ratio in the aqueous phase, the HCL, H^+ and Cl^- concentrations and the equilibration time. In addition extraction of platinum was also found to be dependant on its oxidation state in the aqueous phase. Detailed studies on the effect of these various conditions enabled us to propose a simple but feasible extraction mechanism for both systems. AAS provided a means of studying the systems in detail.

It is now evident that in systems of this kind transfer of platinum/palladium-tin complexes in the form of anions ion-paired to oxonium cations form the basis of the extraction process. The stoichiometry of the complexes so extracted was shown to be dependent on the Sn(II):Pt(II) ratio in the aqueous phase.

CHAPTER 7

CHAPTER 7

7. EXPERIMENTAL

7.1 Chemicals, Reagents and Glassware

Commercial grade nitrogen supplied by Afrox, Cape Town and purged of oxygen by passing it through a chromous chloride solution and distilled water before use [99], was used throughout the course of this work.

Double-distilled water, initially boiled for 30 - 45 minutes in a heating mantle to remove the dissolved carbon dioxide and oxygen, was cooled and saturated with nitrogen and stored in a glass aspirator fitted with a nitrogen inlet. This water was used in the preparation of all aqueous solutions.

Concentrated A.R. hydrochloric acid and methyl isobutylketone (MIBK) were degassed by passing nitrogen through them for 15 - 20 minutes. Analar n-hexane (boiling point range 62 - 82°C) was refluxed and saturated with nitrogen before use.

All chemicals and reagents used for experimental work were analytically pure and obtained from various suppliers. K_2PdCl_4, K_2PtCl_4, Na_2PdCl_4 and Na_2PtCl_4 (5.05 w/w solution) were all obtained from Johnson Matthey Chemicals Limited, Hertfordshire and $SnCl_2.2H_20$ from Hopkins and Williams Ltd., England. H_2PtCl_6, La $(NO_3)_3.6H_20$, $LaCl_3.xH_20$, $Na_2B_40_7.10H_20$, $Cu(NO_3)_2.3H_20$, $Co(NO_3)_2.6H_20$, $Fe(NO_3)_2.9H_20$ and $Ni(NO_3)_2.6H_20$ were all supplied by E. Merck, Darmstadt. $HC10_4$ and NH_4Cl was supplied by BDH Chemicals, England and $U0_2$ was obtained from Koch-Light Laboratories Ltd. in Colnbrook, England. Potassium iodate was dried for 1 hour at 100°C and stored in a desiccator.

Aqua Regia was prepared from A.R. HNO_3 and HCL in the ratio 1:3 [100] and hydrochloric/perchloric acid concentrations were accurately determined by standardising with sodium tetraborate.

A mixture of A and B grade glassware was used. Platinum, palladium and tin solutions were dispensed with piston burettes fitted with a nitrogen inlet. The organic phases, containing various percentages of MIBK in hexane and prepared beforehand by mixing appropriate volumes of hexane and water-saturated MIBK, were stored under nitrogen in amber-coloured bottles. Mettler and Sartorius four decimal balances were used for all weighings.

7.2 Atomic Absorption of Platinum

Platinum stock solutions were prepared by dissolving solid K_2PtCl_4 or Na_2PtCl_4 solution in the appropriate hydrochloric acid concentration and used the day after preparation. $La(N0_3)_3$ stock solutions of 20000ppm were 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 the range 0-120 ppm at the appropriate acid concentration, with additions of tin(II) in a ratio to match the sample matrix as closely as possible. All samples and standards were run on the same day of preparation and standards were freshly made for each extraction.

The Perkin Elmer 5000 atomic absorption spectrophotometer was used for all measurements. Strongly oxidising air-acetylene flames were used for the analysis of platinum with the following spectrophotometer settings:

Lamp Current / mA : 10
Wavelength / nm : 265.9
Slit Width / nm : 0.2

Percentage extraction of platinum in each sample was calculated from a blank value in the following way:

$$\frac{[Pt]_b - [Pt]_s}{[Pt]_b} \times 100$$

where $[Pt]_b$ = concentration of platinum in blank
$[Pt]_s$ = concentration of platinum in sample

7.3 Atomic Absorption of Palladium

Palladium stock solutions were prepared by dissolving K_2PdCl_4 or Na_2PdCl_4 in the appropriate hydrochloric acid concentrations. $La(NO_3)_3$ and $LaCl_3$ stock solutions of 50000 ppm (as recommended by the Perkin Elmer Instructions Manual) were 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 0.5%.

UO_2 was also tested as an interference suppressant. 50000 ppm UO_2 stock solutions were prepared by dissolving the solid in 10 ml of *aqua regia,* warming gently and diluting to volume with appropriate amounts of dilute acid and water. All three interference suppressants were used the day after preparation.

Sets of standards were prepared for palladium in the range 0-70 ppm at the appropriate acid concentration with additions of tin(II) in a ratio to match the sample matrix as closely as possible. All samples and standards had to be run on the same day of preparation since precipitation occurred on prolonged standing.

All measurements were made using a Perkin Elmer 5000 spectrophotometer with strongly oxidising air-acetylene flames and the following spectrophotometer settings:

Lamp Current / mA	: 30
Wavelength / nm	: 276.3
Slit Width / nm	: 0.2

Percentage extraction of palladium in each sample was calculated from a blank value in the following way:

$$\frac{[Pd]_b - [Pd]_s}{[Pd]_b} \times 100$$

where $[Pd]_b$ = concentration of palladium in blank
$[Pd]_s$ = concentration of palladium in sample

7.4 Atomic Absorption of Platinum with Palladium

Platinum-containing-palladium stock solutions were prepared by dissolving both K_2PtCl_4 and K_2PdCl_4 together in the appropriate hydrochloric acid concentration. Sets of standards were prepared for both platinum and palladium in the required range at the appropriate acid concentration using various amounts of the platinum/palladium stock solution. Appropriate volumes of tin(II) stock solution was added in a ratio to match the sample matrix as closely as possible. Flame conditions and spectrophotometer settings for platinum and palladium in the presence of each other were identical to those chosen for the analysis of these metals individually. Percentage extraction of platinum and palladium was calculated using the same methods given on pages 97 and 98 respectively.

7.5 Atomic Absorption of Tin

Stannous chloride stock solutions of appropriate strength were made by dissolving the solid in concentrated, degassed HCL, allowed to stand tightly stoppered for ± 10 - 15 minutes in a beaker containing warm water until the cloudiness disappears, cooled and then diluted to volume with boiled-out, degassed distilled water. Stock solutions were used the day after preparation.

Sets of standards were prepared for tin in the required range at the appropriate acid concentration by adding portions of the tin(II) stock solution to the platinum, palladium or platinum-containing-palladium standards in a ratio to match the sample matrix as closely as possible. All samples and standards were run on the same day of preparation and standards were freshly made for each extraction.

The Perkin Elmer 5000 spectrophotometer with a strongly reducing air-acetylene flame and the following conditions was used for all measurements:

Lamp Current / mA: 20
Wavelength / nm : 286.3
Slit Width / nm : 0.7

Percentage extraction of tin in each sample was calculated from a blank value in the following way:

$$\frac{[Sn]_b - [Sn]_s}{[Sn]_b} \times 100$$

where $[Sn]_b$ = concentration of tin in blank
$[Sn]_s$ = concentration of tin in sample

7.6 Potassium Iodate Oxidations

Stannous chloride solutions used were prepared as described before in Section 7.5. Potassium iodate solutions of appropriate strengths were made by dissolving the dried solid in boiled-out, degassed distilled water.

All titrations were performed under nitrogen using an Erlenmeyer flask fitted with a special bung (Figure 7.1). The method given by Vogel [82] was used for the standardisation of tin(II) solutions throughout this work.

In the titration of a tin(II) solution, portions containing 2.5 ml tin(II) solution were transferred with a piston-burette to the titration flask, previously flushed out with nitrogen. This was followed by the addition of 10ml degassed concentrated HCL, 10ml boiled-out degassed distilled water and 6ml A.R. chloroform with Pasteur pipettes through a hole in the bung to the titration flask. At this stage both aqueous and organic phases were

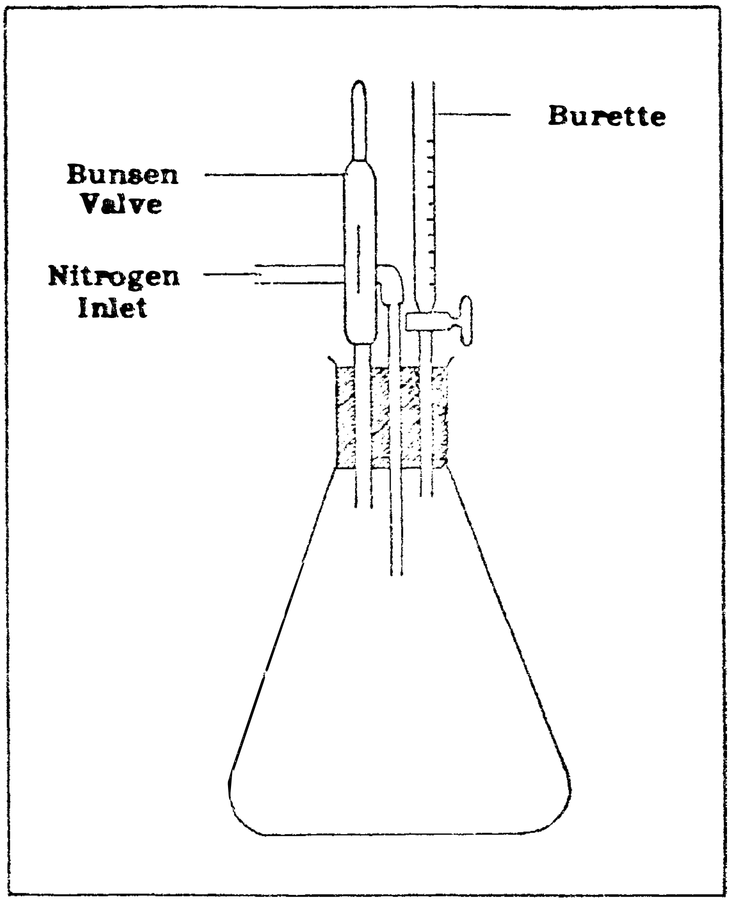


Figure 7.1 Flask with adapted bung for titrations under nitrogen

colourless. However, during addition of the potassium iodate both the aqueous and organic phases underwent a number of colour changes.

On addition of about 60-70% of the required volume of iodate, the aqueous layer became reddish-brown and the chloroform layer acquired a violet colour due to iodine. Addition of smaller increments of the iodate solution followed by vigorous shaking of the stoppered flask caused the organic layer to go faintly violet. The titration was continued with the dropwise addition of iodate solution. The end point is marked by the disappearance of the last trace of violet colour from the organic phase. The aqueous phase was pale-yellowish in colour due to the presence of iodine monochloride.

7.7 Ultraviolet-visible Spectrophotometry

Appropriate volumes of diluted palladium and tin(II) stock solutions in a 1:10 ratio were rapidly transferred, with a microsyringe, to quartz spectrophotometric cells previously flushed out with nitrogen and then tightly stoppered to exclude air. Spectra were run at 3 different acid concentrations viz. 1.5, 1.8 and 2.4M HCL using 10 mm cells, and scans were repeated every 5 minutes. 1.5M, 1.8M and 2.4M HCL were used as blanks for the 3 determinations. A spectrum of palladium alone was also run.

A Superscan 3 Varian Ultraviolet-visible spectrophotometer was used. Spectra were run between 300 and 700 nm using a slit width of 1.5 nm and a scan speed of 200 nm/min.

7.8 Solvent Extraction Procedures

The platinum or palladium and tin solutions were prepared as described in the required HCL concentration. Tin solutions were made up according to the highest desired Pd(II) or Pt(II):Sn(II) ratio. The concentration of tin(II) present in tin stock solutions was checked before extraction by titration with KIO_3. Equal volumes of organic and aqueous phases were used in the extraction.

The metal solutions were dispensed with piston burettes into an extraction tube previously flushed out with nitrogen. After making up to the desired aqueous phase volume with acid, the tubes were sealed with tightly fitting rubber "suba-seals" and the aqueous phase was equilibrated by shaking on a Griffin automatic flask shaker for:

(a) 20 minutes for platinum-tin or platinum-palladium-tin solutions

(b) 15 minutes for palladium-tin solutions

After equilibration, appropriate volumes of various MIBK-hexane (% v/v) mixtures were added to the extraction tubes. The tube was once again tightly sealed and the mixture shaken for

(a) 10 minutes for platinum-tin-MIBK/hexane or platinum-palladium-tin MIBK/hexane mixtures

(b) 5 minutes for palladium-tin-MIBK/hexane mixtures.

Subsequent to extraction, 1 ml of the aqueous phase was removed with a pipette for analysis with the minimum delay. In each set of experiments a blank consisting of an aqueous phase at the same Sn:Pt ratio as the samples was run.

Experiments to determine the effect of HCL concentration on the extraction were carried out by adding varying amounts of concentrated HCL to the aqueous phase to give the desired acid concentration. Varying amounts of NH_4Cl were added directly to the extraction tubes when making a study of the effect of Cl^- concentration on the extraction. Determination of the effect of H^+ concentration on the extraction was carried out by adding appropriate volumes of $HC10_4$-HCL solutions of varying strengths to the extraction tubes to give the desired H^+ concentrations.

Solutions containing the base metals Co, Cu, Fe and Ni as their nitrates were prepared by dissolving them together with K_2PtCl_4 and K_2PdCl_4 in the appropriate hydrochloric acid concentration. These solutions were used in our preliminary interference study of the base metals on the separation of platinum and palladium.

In order to demonstrate mass balance for platinum and tin, it was essential to know how much of both metals were present in the remaining organic phase. Because of the problems associated with the direct analysis of the organic phase by AAS, we decided instead to back-extract the red Pt-Sn complex into an aqueous acid phase by swamping the organic phase with hexane. The back-extraction procedure is rather tedious, time-consuming and tiring, nevertheless, results obtained have shown it to be a remarkably successful method for demonstrating mass balance of both platinum and tin. (See Appendix 1).

APPENDIX

APPENDIX 1

(a) Platinum

% MIBK	% Mass Balance	Relative percentage error
0	99	1.0
40	99	1.0
50	101.4	1.4
60	100.9	0.9
75	101.6	1.6
100	99	1.0

(b) Tin

% MIBK	% Mass Balance	Relative percentage error
50	98.4	1.6
65	101.4	1.4
75	99.2	0.8
90	102.2	2.2
100	102.6	2.6

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