SOLVENT EXTRACTION OF Pt(IV) AND Pd(II) WITH 7-SUBSTITUTED 8-HYDROXYQUINOLINE DERIVATIVES

by

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Solvent extraction of Platinum and Palladium

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Abstract

Extensive characterization (IR, UV, ^{1}H-NMR and GC-MS) of new, non commercially available 7-substituted-8-hydroxyquinoline derivatives, 8-HQ, labelled TN 1911, TN 2181, TN 2221 and TN 2336, manufactured by Schering Berlin AG., (Germany) is reported. Hydrochloric acid and the accompanied water extraction performance of Kelex 100, TN 1911 and Lix 26 as well as the occurrence of protonated extractant in the organic phase is also discussed.

Equilibrium measurements of palladium and platinum extraction by chloroform solutions of 7-substituted-8-hydroxyquinoline derivatives from aqueous chloride media demonstrated that Pd(II) is extracted as the chelate PdQ_2 whereas Pt(IV) is extracted as the ion-pair $PtCl_6^{2-} \cdot (H_2Q^+)_2$. The formation of the chelate PdQ_2 was also confirmed with direct spectroscopic analysis. The extraction equilibrium constants, K_{ex}, were determined. It is shown that metal extraction is influenced by both the extractant concentration and reagent structure. The importance of steric over electronic effects with respect to metal extraction is discussed. The individual effects of Pd(II), Pt(IV), proton and chloride ion concentration on metal extraction are quantified. It was found that Pd(II) and Pt(IV) extraction reactions are exothermic. The influence of stripping agent composition with respect to palladium stripping was investigated as well.

Extraction and stripping kinetics of palladium by chloroform solutions of 8-hydroxyquinoline derivatives from aqueous chloride media are reported. It is shown that the extraction of Pd(II) proceeds via the fast formation and interphase transfer of the ion-pair $PdCl_4^{2-} \cdot (H_2Q^+)_2$ and the slow homogeneous transformation of the latter into the PdQ_2 chelate. The rate laws for the extraction and stripping reaction of $PdCl_4^{2-}$ with 8-HQ were determined.

Finally, it is demonstrated that an exchange reaction takes place between Pd(II) and Pt(IV) when both metals are extracted from a mixed metals solution.

Résumé

La caractérisation de nouveaux dérivés de la quinolinole-8, indentifiés TN 1911, TN 2181, TN 2221 et TN 2336 fabriqués par la firme Schering Berlin AG., (Allemagne) est raportée. Ces dernier ne sont pas disponible commerciale- ment. Aussi, les quantitées d'eau et d'acide chloridrique co-extractaient par ces dérivés a été déterminées.

Des mesures à l'équilire ont démontrées que le palladium et le platine sont extraient respectivement, en milieu aqueux fortement chloré, sous forme de complexe chélaté (PdQ_2) et de paire d'ion ($PtCl_6^{2-} \cdot (H_2Q^+)_2$). De plus, l'existance du complexe chélaté a été confirmée à l'aide de la spectroscopie Ultra-Violet. Les constantes d'équilibres pour l'extraction du Pd(II) et du Pt(IV) en milieu HCl sont raportées. L'importance et le rôle de l'emcombrement stérique vis-à-vis l'extraction et la ré-extraction du Pd(II) et du Pt(IV) est discuté. De plus, l'effet de la concentration en Pd(II), Pt(IV), H^+ et Cl^- sur l'extraction de ces métaux a été évalués. L'extraction du platine et du palladium sont des réactions exothermiques. L'importance de la composition des solutions de ré-extraction à été étudiée.

La cinétique d'extraction et de ré-extraction du palladium, en milieu choré, à été étudiée. Le mechanisme d'extraction du palladium implique, dans un premier temps, la formation rapide d'une paire d'ion ($PdCl_4^{2-} \cdot (H_2Q^+)_2$) suivie d'une lente transformation en complexe chélaté (PdQ_2). Cette dernière se déroule dans la phase organique. De plus, les constantes de vitesse pour l'extraction et la ré-extraction du palladiun ont été déterminées.

Finallement, il est démontré qu'une réaction d'échange se produit, dans la phase organique, entre le platine et le paladium lorsque ces deux métaux sont présent en solution aqueuse. L'extraction du palladium conduit à la formation d'un complexe thermodynamiquement plus stable.

Foreword

McGill University offers the option to Ph.D. candidates to use published papers as whole parts of their theses. This thesis has in fact been prepared following this option. In accordance with guidelines ("Guidelines Concerning Thesis Preparation", Faculty of Graduate Studies and Research Revised 05/92), the following text is quoted:

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This dissertation contains seven chapters, four of them are papers already published or accepted or submited for publication. Chapter 1 and 2 are the introduction and the literature review respectively. Chapter 3 is the paper dealing with the characterization of the new 8-hydroxyquinoline derivatives and the extraction of HCl and water. Chapters 4 and 5 are two articles describing the extraction and stripping equilibria of Pd(II) and Pt(IV) from chloride media respectively. Chapter 6 is the paper dealing with the kinetics of Pd(II) extraction and stripping. Finally, chapter 7 summarizes the thesis with the overall conclusions and claims to originality. It should be clearly stated here that due to the chosen thesis format, i.e. whole chapters to be copies of papers published or accepted for publication, some minor duplication has inevitably occurred. Thus the introduction in Chapters 3, 4, 5 and 6 is to a great extent common to all these chapters and each starts with an Abstract which is a standard feature of all published papers.

According to the normal procedure, all papers have been submitted for publication in refereed scientific journals, with the research director, Dr. G. P. Demopoulos, as a co-author. Nevertheless, all of the work has been done by the author of this thesis, with the exception of the normal supervision and advice given by the research director.

The papers which form Chapters of this thesis are the following:

Chapter 3: "New 8-Hydroxyquinoline Derivative Extractants for Platinum Group Metals Separation. Part 1: "Characterization and HCl Extraction". Solvent Extraction and Ion Exchange 11(2), (1993), p. 349

Chapter 4: "New 8-Hydroxyquinoline Derivative Extractants for Platinum Group Metals Separation. Part 2: "Pd(II) Extraction Equilibria and Stripping". Solvent Extraction and Ion Exchange 14(2), (1994), (in press)

Chapter 5: "New 8-Hydroxyquinoline Derivative Extractants for Platinum Group Metals Separation. Part 3: "Pt(IV) Extraction Equilibria and Stripping". Solvent Extraction and Ion Exchange 14(3), (1994), (in press)

Chapter 6: "New 8-Hydroxyquinoline Derivative Extractants for Platinum Group Metals Separation. Part 4: "Kinetics of Pd(II) Extraction and Stripping ".Solvent Extraction and Ion Exchange, Submitted (1994).

I hereby give copyright clearance for the inclusion of the following papers, of which I am the co-author, in the thesis of Bruno Côté.

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Nomenclature

D	distribution coefficient	(-)
$K_{Pt, ex}$	Pt (IV) extraction equilibrium constant	(-)
$K_{Pd, ex}$	Pd (II) extraction equilibrium constant	(L^4 mol^{-4})
k_{osb}	observed rate constant	(s^{-1})
k_{ext}	extraction rate constant	(s^{-1})
k_{strip}	stripping rate constant	(s^{-1})
K_p	equilibrium constant of protonation reaction	(L mol^{-1})
K_{ip}	equilibrium constant of ion-pair formation reaction	(L^2 mol^{-2})
M	concentration	($molL^{-1}$)
r	rate	(mol L^{-1} s^{-1})

Subscripts

org	organic species
0	initial time
t	time t
obs	observed
p	protonation
ip	ion-pair
net	net

Contents

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[1] Due to limitations imposed by the wordprocessor the Figure captions appearing in this thesis are abbreviated versus of the captions appearing in this section. The reader is to refer to this section for full details about each Figure.

Figures appearing in Appendices

List of Tables

Chapter 1

Introduction

1.1 Chemistry and Mythology (1)

Many great chemists not only had a good sense of humour but also they were well acquainted with mythology and the humanities. Thus several metals were named after Greek, Roman, German and Scandinavian mythology. In the case of palladium, when the ancient Greek city of Troy was built, Ilos who founded the city asked Zeus to send a sign of his favour. The next day Ilos found an image of Pallas Athena, goddess of wisdom, (name given to Minerva in Greece from which the city Athens was named) which the great god had sent down from the heaven. This statue was treasured in the city as palladium, or safeguard. It was believed that as long as the palladium remained in the city, Troy could not fall. The Greeks had learned of the existence of palladium and were determined to gain possession of it. They tricked the Trojans by the wooden figure of a horse inside which they had placed a contingent of soldiers. When a minor planet was discovered in 1803 by the German astronomer Heinrich Olber he named it Pallas and a year later the English chemist William H. Wollaston discovered a new metal in crude platinum which he called palladium.

1.2 The Occurrence of PGM

Native platinum was discovered by Europeans in the alluvial deposits at the Choco River in Colombia around 1557 (2), but remained unknown to European society until the report by Brownrigg and Watson before the Royal Society in 1750. According to other sources (3) platinum (the name of which) is derived from the Spanish word platina, which means silver, was discovered in South America by Ulloa in 1735 and by Wood in 1741. The metal was most likely used by pre-Columbian Indians before its "discovery" by the Europeans. In 1752, Schaffer, in Sweden, discovered that platinum could be dissolved in *aqua-regia* and Marggraff found that addition of ammonium chloride produced a precipitate of ammonium hexachloro platinate. This process is still one of the standard ones in the platinum refining industry (4).

The platinum group metals (PGM) include in addition to platinum palladium, rhodium, iridium, osmium and ruthenium. Together with gold and silver they form the family of precious metals. They occur in nature associated with the major base metals iron, copper, cobalt and a wide range of minor elements such as lead, tellurium, selenium and arsenic. The occurrence of PGM in the earth crust (4,5) is about one-hundredth of a part per million (ppm). Even in platinum-rich deposits (e.g. the Merensky Reef in Transvaal, South Africa) where the PGM concentration is a thousand times higher, it reaches only 10 ppm. Early production of PGM in Colombia was followed by discoveries of gold and platinum in the Ural mountains in Russia in 1822, platinum and iridium in Good New Bay, Alaska, platinum arsenide (sperrylite) in Sudbury, Ontario (1875) and sperrylite, copperite and baggeite (sulphide minerals) in South Africa (1929). Today, about 80 per cent of the world's reserves of the PGM are believed to be concentrated in the gigantic geological structure know as the Bushveld Igneous Complex in South Africa (6). A special issue of the Journal of Economic Geology was devoted to the subject of platinum deposits of the world (7). The estimated reserves of PGM for 1987 and the current production by the major producers and the estimated expansion capacity have been reported by Warshawsky (8). According to this author the total world PGM reserves were estimated, in 1987, to be 87 500 ton.

1.3 The Solvent Extraction Technique

The growing demand for highly pure precious metals to be used in high-tech applications, the need for modern and clean processes and the increasing volume of low grade PGM from secondary sources available for recycling, impacts directly today on the industrial practice of recovering and refining precious metals. Refining of PGM consists of several stages: (i) ore concentration by physicochemical techniques such as flotation (ii), pyrometallurgical concentration producing copper-nickel sulfide matte, and hydrometallurgical concentration producing leach and electrorefinery sludge and (iii), final refining to produce the individual PGM. The present study concentrates on the last stage, i.e. the final refining stage, of this overall process. Separation and recovery of PGM has traditionally been achieved through a series of chemical salt precipitation-dissolution steps followed by calcination to produce pure metal or sponge (9). To meet the new challenges, the industry is abandoning the inefficient classical techniques and is adopting modern separation methods. Among the latter, solvent extraction (SX) proves to be the most suitable and powerful separation technique for PGM. Thus today major refineries operate SX circuits while others test and plan the introduction of SX technology in their own operations.

SX is a separation technique in which a solute is transferred from one liquid phase to another liquid which is in contact with the first. In hydrometallurgy, the aqueous phase contains the metal which is to be concentrated into the organic phase. SX owes its origins to analytical chemistry in which dilute aqueous solutions are concentrated using an extractant reagent in the organic phase. Thus oxine (8-hydroxyquinoline) since 1929, dithizone in 1937 and phenanthroline since 1941 are known as very good extraction reagents. The industrial use of SX was pioneered in 1944 by the nuclear industry (10-13). This was the forerunner of a large number of applications of SX not only in the nuclear industry but in many other industrial fields.

Solvent extraction is widely practised nowadays in hydrometallurgy. It was during the 60's that effective extractants became commercially available and made possible the industrial expansion of the process. Since that time extensive research has been carried out which has led to the development of several new selective extractants. Nowadays, the search for new improved reagents and for new applications (metal selectivity) of existing reagents continues although at a slower pace. The regular international solvent extraction conferences (ISEC), held every three years, is a very good indication of the importance and success of this powerful and versatile separation process.

1.4 The Scope of this Work

The analytical importance of 8-quinolinol, also called 8-hydroxyquinoline (8-HQ) or oxine is now very well established (14-17). Oxine has the particular ability to form stable complexes, called oxinates, with several metallic ions. The references (14-17) also include an extensive review of the physical, chemical and spectroscopic properties of 8-HQ and its various derivatives. The synthesis of 8-HQ and its derivatives has also been reported (17,18).

The search for new reagents seems to be slowing down. This may be due to the exorbitant cost associated with fundamental research such as the synthesis and the testing of the physical, chemical and toxicological properties that must be done prior to the commercialization of the extractant. Therefore the actual trend is to find new applications for the already existing reagents. They can be used either alone or as mixtures to obtain interesting synergistic effects.

Unfortunately, most of the SX processes for PGM make use of reagents which are commercially available but not especially developed for the PGM industry. It is the purpose of this work to study a series of novel reagents of alkylated 8-hydroxyquinoline derivatives called TN 1911[1], TN 2181, TN 2221 and TN 2336 which have been specifically designed to meet the particularities of the solution chemistry of Pt(IV) and Pd(II) and to compare their performance *vis-à-vis* other 8-HQ derivatives commercially available, i.e. Kelex 100[2] and Lix 26[3].

The principal objectives of the present work were (i) the characterization and comparative evaluation of these new 7-substituted 8-hydroxyquinoline (8-HQ) as platinum and palladium extractants and, (ii) the study of the fundamental chemistry of Pt(IV) and Pd(II) separation from chloride solution with 8-HQ reagents. The present study constitutes an extension of earlier process development studies undertaken by McGill University, CANMET and Noranda Technology Centre which have led to two patents (19,20)

The work that is described in the present thesis is organized in the following manner. The reagents used throughout this investigation are extensively characterized in chapter 3. In the same chapter the extraction of hydrochloric acid and water by Kelex 100, TN 1911 and Lix 26 is also discussed. In chapters 4 and 5, the equilibrium measurements of palladium and platinum extraction, by chloroform solutions of 7-substituted 8-hydroxyquinoline derivatives from single metal chloride aqueous solution are reported. In addition to chloroform solutions, solvents composed of extractant-tridecanol-Solvesso 150[4] were also tested as it is this solvent composition that is the preferred industrial formulation. Chapter 6 describes the kinetics of Pd(II) extraction and stripping and the behaviour of Pd(II)

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[1] Theses reagents were experimental products developed by the Chemical Company, Schering Berlin Bergkamen A.G., Germany.

[2] Proprietary product of Sherex Chem. Company, Dublin Ohio, USA. As of september 1992 Kelex 100 is property of the WITCO Chemical Company USA.

[3] Proprietary product of Henkel Corporation USA.

[4] Proprietary product of Exxon Chemicals Ltd. USA.

and Pt(IV) when both metals are co-extracted.

1.5 References

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Chapter 2

Literature survey

2.1 Introduction

In this chapter a general survey of the literature published on the subject is presented. Historically, early commercial refining processes have been applied to gold refining. Sir T.K. Rose (1) in 1906, A.E. Richards (2) in 1949 and more recently Nadakarni et al. (3) among others have outlined some of the very early commercial gold refining processes, namely; the nitric acid, the sulphuric acid and the *aqua-regia* processes.

Nowadays, three major refineries: International Nickel (INCO), Matthey-Rustenburg Refiners (MRR) and Lonrho, are operating hydrometallurgically-based processes for the separation of precious metals. The largest of the Canadian precious metal producers, INCO has developed its own process for its refinery in Acton England. MRR use a route developed on their behalf by Johnson Matthey in England whilst both their South African competitors, Impala and Western (Lonrho refinery) use a flowsheet developed by the Council for Mineral Technology (MINTEK) of South Africa. These processes have been compared and discussed periodically since 1982 by Edwards and te Riele (4), Flett (5) and more recently by Harris (6).

The present chapter is divided in four sections. The first one described the solvent extraction-based process flowsheet employed by the major precious metal refiners. In the same section some fundamental studies published recently describing the chemical reactions involved in those processes are also reviewed.

The second section presents new process schemes which can potentially find industrial applications. The third one outlines the other non-precious metal applications of Kelex 100 and finally, the last section summarizes the previous research work performed at McGill University related to the extraction of precious metals.

2.2 Precious Metal Industrial Applications of Solvent Extraction

2.2.1 The INCO Refinery

Historically, INCO was the first to employ solvent extraction commercially in PGM processing. The particular precious metal concentrates processed by INCO are derived from the very large scale nickel and copper mining operations of the parent company in Canada. At the end of copper and nickel processing, PGM collect in the anode slimes. The PGM content of the latter are further enriched before separation of the six PGM (Pt, Pd, Rh, Ru, Ir and Os) including also gold and silver. The classical method for the refining of gold has been reported by Rimmer (7).

Solvent extraction, at that time, was limited to the recovery of gold. The process was developed out of a research project at Burnel University in U.K. (8). The small SX plant using dibutyl carbitol (DBC) was commissioned in September 1971. The selection of DBC was made because of its low volatility (b.p. 255 °C), high flash point (118 °C) and low solubility in water (0.3% at 20 °C) and of course its good extraction properties for gold. DBC is also commercially known as Butex but from a systematic nomenclature point of view it should be called diethylene-glycol dibutyl ether.

The flowsheet of the separation of gold with DBC is shown in Figure 2.1 (7). Gold extraction from HCl solution by DBC is quantitative and selective with respect to other precious metals. Although DBC does not extract platinum metals from chloride solutions, other base metals are co-extracted to some degree. For example Rimmer (7) has reported that the two major co-extracted impurities at 3.0M HCl are Sn(IV) and Fe(III). Small amounts of As(III), Sb(V) and Te(IV) may also be present in the loaded extractant. Therefore, a scrubbing stage with 1.5M HCl is employed to eliminate all impurities present in the loaded organic. Finally gold is recovered from the loaded solvent by a *in situ* reduction of the metal by an aqueous solution of oxalic acid.

The feed composition used by INCO during their pilot plant tests was the following (7): Au 4-6 g/L, Pt 25 g/L and Pd 25 g/L, small amounts of Rh, Ru and Ir and 20g/L of base metals. Finally, the solution contained 3.0M hydrochloric acid and the total chloride ion concentration was 6.0M. Gold extraction was very quantitative and up to 25 g/L of gold could be loaded in the undiluted organic phase. Furthermore, equilibrium tests showed that it was possible to produce a raffinate containing less than 1 ppm of gold in a single contact with equal volume of both phases (A/O=1). In fact, with a gold content of 4-6 g/L in the feed, the A/O ratio could be as high as 6:1.

According to spectroscopic studies by Seargent and Rice (9) gold is extracted as a square planar complex, in other words the gold complex in the organic phase is similar to that in the aqueous phase, and the selectivity of DBC for gold is due to the low charge to size ratio of this complex. According to the same study the extracted species present in the organic phase is the monosolvated complex $HAuCl_4{\cdot}DBC$ (9). The extraction reaction is described as follows:

$$AuCl_4^- + HCl + DBC_{org} \rightleftarrows [HAuCl_4{\cdot}DBC]_{org} + Cl^- \qquad (2.1)$$

It was also noted that the tetrachloroauric species loaded in the DBC solvent has

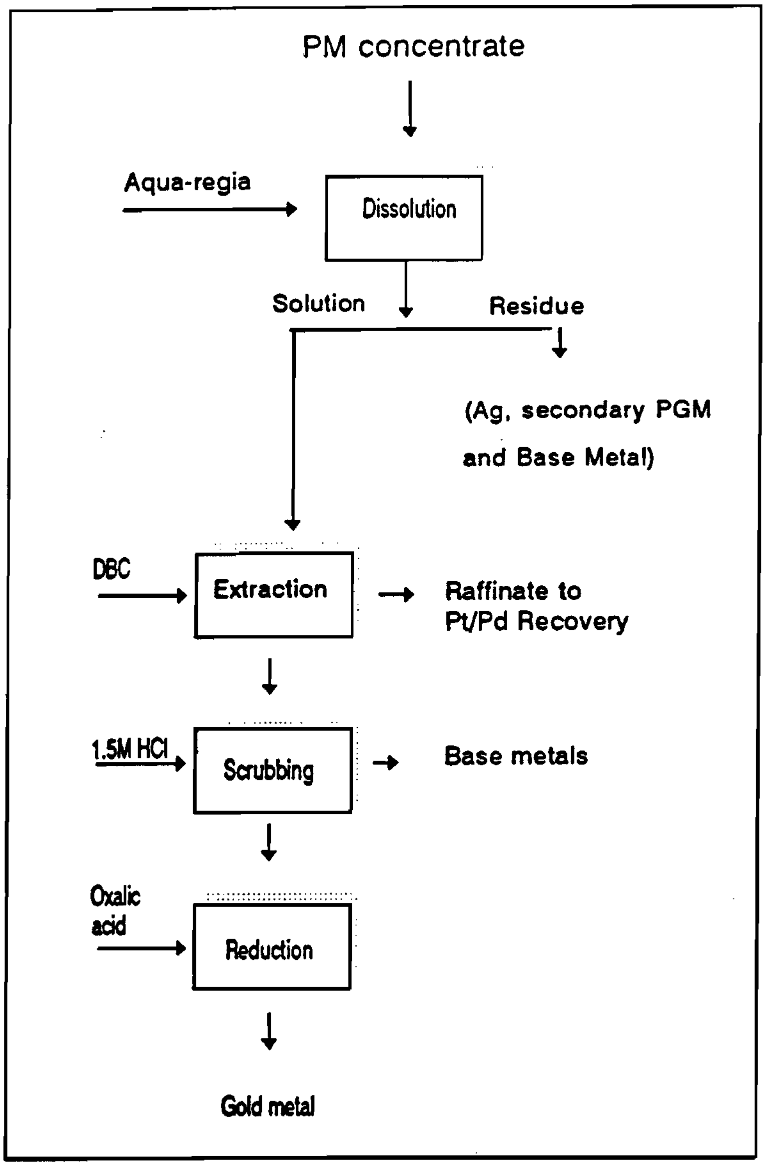

Figure 2.1 The original INCO flowsheet for the separation and recovery of gold with SX (7).

an extremely high stability constant, which thus permits the effective scrubbing of the loaded extractant with 1.5M HCl.

It is this high stability of the extracted complex that makes the stripping of gold with water non effective as reported by Rimmer (7). Thus a novel stripping technique had to be developed involving reduction of Au(III) to metal through contact of the loaded DBC with an aqueous solution of oxalic acid. The kinetics of that reductive stripping reaction have been studied by Reynolds et al. (10). They found that such reaction was first order with respect to both the concentration of gold extracted and that of the reducing agent, thus giving an overall second order reaction. The same investigators tested several other reducing agents and established the following order according to speed of reduction: hydrogen peroxide > hydrazine hydrate > sodium nitrite > formic acid > oxalic acid. According to this study hydrogen peroxide is the most effective of all reductants tested which gives complete reduction (70-80°C) in about 30-60 minutes, compared to 3-5 hours for oxalic acid. However, hydrogen peroxide leads to the formation of a gold sponge whereas oxalic acid reduction produces a gold sand and; all other reducing agents tested gave flakes. This study also demonstrated that the reduction reaction took place in the aqueous phase. Therefore, the presence of water is necessary to effect the reaction. Finally, the reductive stripping with oxalic acid required slightly more oxalic acid than indicated by the stoichiometry of the following reaction:

$$3(COOH)_2 + 2[HAuCl_4 \cdot DBC]_{org} \rightleftarrows 2DBC_{org} + 2Au^{\circ} + 6CO_2 + 8HCl \quad (2.2)$$

The plant was initially operated batch-wise rather than continuously. Such operation was necessary in order to allow for more flexible interfacing with the up- and down-stream processing steps. The extraction was carried out in a 600 L glass-lined Pfaudler vessel and a 90 rev/min variable-baffled stirrer was used. After extraction and separation of the raffinate phase the loaded organic was kept in the vessel and subjected to three successive scrubbing contacts with 1.5M HCl. The scrubbed organic solution was then transferred to the reduction vessel. The latter operation was conducted under gentle agitation conditions and at a temperature not exceeding 90 °C in order to produce the desired coarse gold sand. After that DBC was recycled to the extraction stage. Both the spent oxalic acid and HCl solutions were treated for recovery of traces of precious metals. The quality of the produced gold was excellent. The major economic down-side reported by Rimmer (7) was the overall loss of solvent. The latter has been evaluated to be as high as 4%.

2.2.2 INCO: The Second Phase at the Acton Plant

The immediate success of the gold process installed in 1971 stimulated INCO research into extractants for other precious metals. By the late 70's a new flowsheet had been developed and piloted (11,12) and commercial implementation started soon after that.

The process developed involves extensive usage of solvent extraction technology. First, total leaching of the precious metals concentrate (except for silver) is achieved by HCl solution and chlorine gas. Metals are then separated from the solution selectively in a straight chain approach. The key to the process is three integrated solvent extraction circuits for gold, palladium and platinum. A simplified flowsheet of the new process has been published (12). Insoluble silver is recovered as AgCl from the leaching step and further refined most likely by selective precipitation. The actual flowsheet is presented in Figure 2.2 (5,11).

Ruthenium and osmium are the first metals separated so as to avoid downstream interferences. Co-distillation of tetroxide is accomplished by raising the pH and adding an oxidant. The distillate is then scrubbed with a dilute HCl solution. Osmium is re-distilled and the residual ruthenium chloride solution is processed to refine ruthenium.

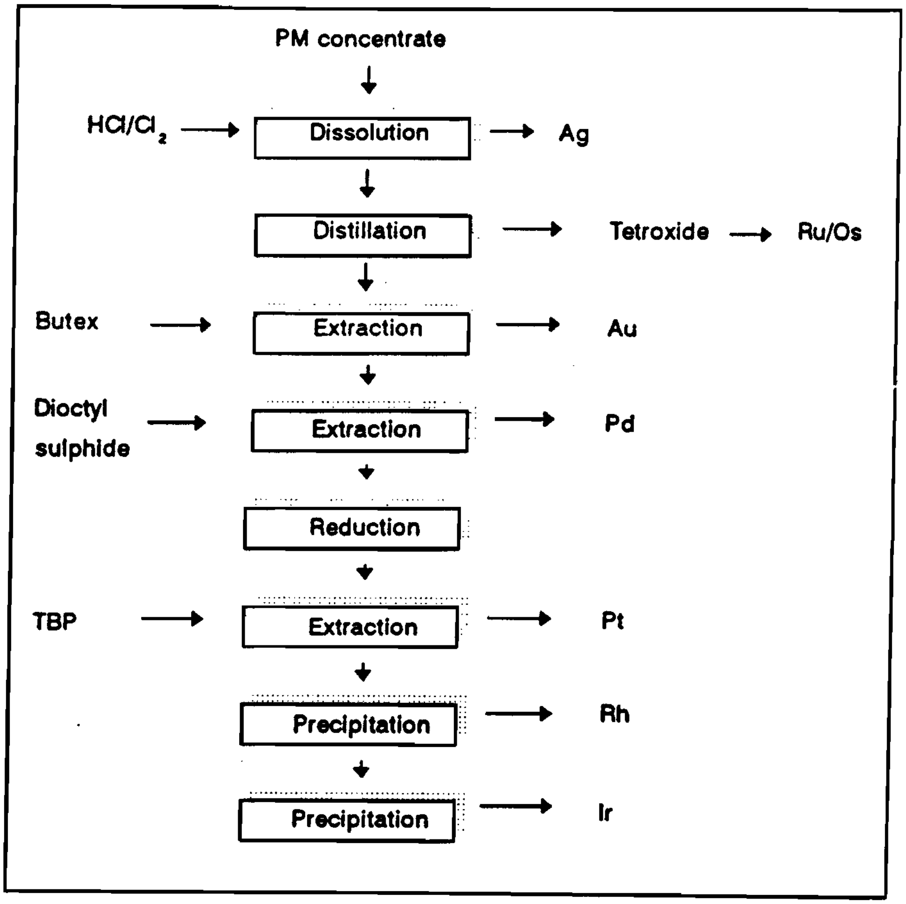

Figure 2.2 The INCO flowsheet for the separation and recovery of PGM at the Acton plant (5,11).

Gold is still recovered by DBC and less than 1 ppm of gold remains in the raffinate. The extraction of gold, scrubbing and stripping in the new flowsheet are basically the same to that already described in the first part. Now however, new multi-stage glass mixer-settlers are used for continuous extraction and scrubbing. The extraction is achieved in two stages whereas the scrubbing requires three stages (13). Finally reductive stripping is still preformed batch-wise as described above yielding > 99.99% pure gold.

Complete elimination of residual organic in the gold-free raffinate is essential before the next step which is palladium extraction. The latter is performed with dioctyl sulfide (25 vol%) in Isopar M (Esso). This extractant has an excellent selectivity with respect to other platinum group metals. However, the extraction kinetics are relatively slow and some base metals are also co-extracted. Due to such kinetics, batch reactors are operated. The loading capacity of dioctyl sulphide is high (32 g/L) producing a raffinate containing less than 1 ppm of palladium with a single extraction step. Daamash et al. (14) have studied the kinetics and extraction mechanism of Pd(II) in hydrochloric acid media with di-n-hexyl sulphide and have found that impurities in the various as-received commercially available extractants interfered with the extraction process. These impurities which were mostly amines act as phase transfer catalysts and tend to increase the extraction rate thus reducing the selectivity of Pd(II) extraction with respect to that of Pt(IV) (15). The extraction of Pd(II) by di-n-hexyl sulphide can be expressed as follows:

$$PdCl_4^{2-} + 2R_2S_{org} \rightleftarrows [PdCl_2(R_2S)_2]_{org} + 2Cl^- \qquad (2.3)$$

where R_2S denotes the extractant.

The loaded organic is then scrubbed with HCl and stripped with ammonia. As pointed out by Harris (6) the use of ammonia as stripping agent implies that the gold content in the feed should be as low as possible. Otherwise gold-ammonia mixtures may form which are potentially explosive. Palladium is recovered from the strip solution by acidifying with HCl to precipitate palladium as diammino palladous chloride. Finally, palladium metal is produced by either direct calcination of the salt or by reduction with sodium formate or formic acid followed by calcination, yielding Pd > 99.95% purity.

Platinum is extracted with tributyl phosphate (60 vol% TBP + 5 vol% isodecanol diluted in Isopar M). Before the extraction the feed acidity has to be adjusted (11) at 5-6M HCl and Ir(IV) is reduced to Ir(III) with sulphur dioxide. At this oxidation state, as Knothe (16) showed, Ir(III) is not extracted. The following reaction (17) describes the extraction of platinum by TBP.

$$PtCl_6^{2-} + 4TBP_{org} + 2HCl \rightleftarrows [(H_3O^+ \cdot 4H_2O \cdot 2TBP)_2PtCl_6^{2-}]_{org} + 2Cl^- \qquad (2.4)$$

Extraction is performed in four countercurrent stages in mixer-settlers, producing a raffinate containing 20-50 ppm of Pt (IV).

The loaded organic is then scrubbed, in two stages, with 5-6M HCl and stripped with water. Platinum is finally recovered by precipitation as diammonium hexachloro platinate by ammonium chloride. The purity of the metal recovered from the salt is better than 99.95%.

At this point in the process the raffinate containing rhodium, iridium and base metals is treated. Iridium is separated by selective precipitation and the resultant chloro-complex purified. The rhodium raffinate is further processed to form a nitrite complex from which base metals are separated, followed by crystallization and ion-exchange chromatography to produce a rhodium chloride solution. Both rhodium and iridium are then recovered by precipitation of their ammonium salts, followed by reduction or calcination.

The purification of rhodium via the formation of the nitrile complex has been published recently by Grant (18). Because, the direct substitution of Rh(III) chloro-complexes by the normal S_N2 mechanism is relatively slow, the latter is catalysed by the addition of a mild reducing agent. The formation of the hexanitritorothate anion ($[Rh(NO_2)_6]^{3-}$])has been used extensively by a number of refiners including INCO (19-21) for the purification of rhodium. This anion is very stable to hydrolysis even under quite strongly alkaline conditions and therefore rhodium can be separated from the majority of base metals as they form insoluble hydroxides or basic salts. Rhodium is then precipitated as a mixed sodium ammonium salt ($Na(NH_4)_2[Rh(NO_2)_6]$). This precipitation is not very selective with respect to other precious metals. This salt is then re-dissolved in HCl to reform the chloro-complex. Rhodium can then be further purified by repeating the nitration step and re-precipitation steps. It is finally recovered as metal by reduction with formic acid.

2.2.3 The Matthey Rustenburg Refinery

The precious metals concentrates processed by the Matthey Rustenburg Refiners (MRR) are derived from copper-nickel sulphide ore. The latter is principally mined commercially in Canada, USSR, and the Merenskey Reef, Transvaal, South Africa (22). According to Reavill and Charlesworth (23) the ore is concentrated by mineralurgical and pyro-metallurgical methods. The concentrate so produced contains generally 50% of PGM but also gold, silver, copper, nickel and base metals.

The MRR flowsheet has already been published and discussed (5,23) and is partially based on Edwards's work (25). As with INCO, the system is oriented towards the complete solubilization of the precious metals. Also, according to Reavill and Charlesworth (23) it appears that the approach used is the straight chain route. In such an approach, each metal is removed from the mixture one at a time. The MRR flowsheet is shown in Figure 2.3 (5).

The typical MRR feed composition is as follows (23): gold 5-7 g/L, platinum 80-130 g/L, palladium 45-65 g/L, ruthenium 10-20 g/L, rhodium 10-20 g/L, osmium 0.1-1 g/L, iridium 1-5 g/L and base metals 50-200 g/L. It is likely that the total solubilization of the concentrate is achieved with HCl/Cl_2.

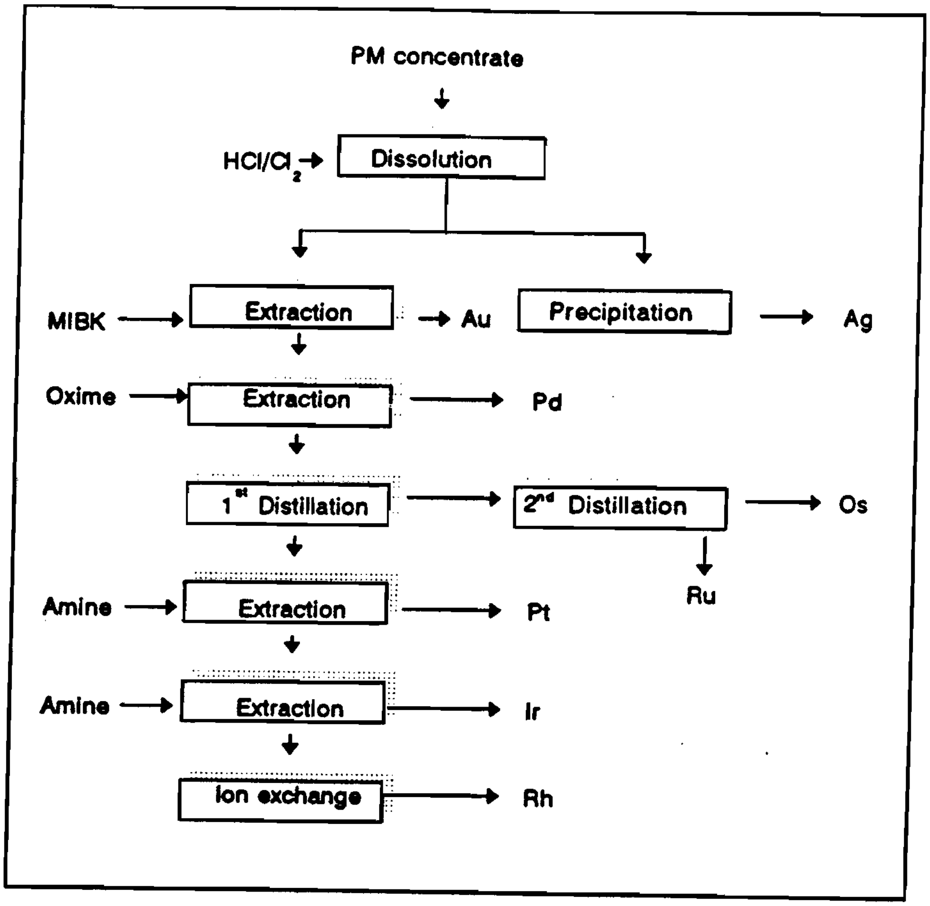

Figure 2.3 The Matthey Rustenburg Refiners flowsheet for the separation and recovery of PGM (5).

Silver is separated by filtration as AgCl and further refined by selective precipitation.

Gold is extracted by methyl isobutyl ketone (MIBK) according to the following reaction.

$$H^+ + AuCl_4^- + xMIBK_{org} \rightleftarrows [HAuCl_4 \cdot xMIBK]_{org} \tag{2.5}$$

However, from the reported flowsheet it is certain that some base metals are co-extracted. The extent of base metal extraction depends on the feed acidity. In the case of MIBK (5) the first extraction stage, performed at high acidity, is highly efficient for base metals extraction, while the second one, done at low acidity is very selective for gold extraction. The loaded solution of MIBK is then scrubbed with dilute acid and gold is finally recovered by reductive stripping (cementation) with iron powder.

Palladium is also separated by SX using a β-hydroxyoxime. Due to its very slow kinetics the latter step has to be performed as a batch operation. Although MRR have not disclosed the exact extractant used it is likely to be, according to Flett (5), a substituted salicylaldoxime manufactured by Henkel Corporation or Acorga. The extraction kinetics can be enhanced by the addition of amines (23) to act as phase transfer catalysis but this leads to a decrease of the extractant's selectivity similarly to the R_2S-Pd(II) system (15) already discussed. The extraction reaction of palladium by oxime (HOX) is presented below (23).

$$PdCl_4^{2-} + 2HOX_{org} \rightleftarrows Pd(OX)_{2org} + 2H^+ + 4Cl^- \qquad (2.6)$$

Since 6M HCl is used to strip palladium it is implied that a chelate complex ($Pd(OX)_2$) is formed as the extracted species in the organic phase. This has been confirmed by Freiser (24). Depending on the feed acidity, copper is co-extracted with palladium. The former is efficiently scrubbed out with dilute acid prior to palladium stripping. Separation factors for palladium over platinum as high as 10^3-10^4 have been reported for the β-hydroxyoxime system (20). Finally palladium purity generally better than 99.9% can be achieved without amine accelerators, otherwise the purity is around 99.5%. Final metal recovery is accomplished by precipitation of the ammonium salt (19) ($Pt(NH_3)_2Cl_2$) as in the INCO process.

Osmium and ruthenium are removed by distillation of their respective tetroxides (OsO_4 and RuO_4) despite the great risks involved in the distillation of such highly toxic compounds. Selective distillation is achieved by the addition of a strong oxidizing agent such as sodium bromate, adsorption into dilute HCl, reduction of ruthenium to the 6+ state followed by a second distillation. An alternative solvent extraction route for ruthenium via the formation of a nitrosyl complex ($RuNOCl_5^{2-}$) has also been reported (25). This complex is extracted with a tertiary amine, stripped with an alkaline solution and then converted by oxidation to RuO_4^{2-} and finally precipitated as RuO_2.

Tri-n-octyl amine (R_3N) is used to extract platinum. The extraction is described below.

$$2[R_3NH^+Cl^-]_{org} + PtCl_6^{2-} \rightleftarrows [(R_3NH^+)_2 \cdot PtCl_6^{2-}]_{org} + 2\ Cl^- \qquad (2.7)$$

The ion-pair formed as the extracted species $[(R_3NH^+)_2 \cdot PtCl_6^{2-})]$ is very stable. Thus, on the basis of distribution coefficient values reported (26) 10-12M HCl has to be used to adequately strip platinum. Also, to avoid iridium co-extraction, its reduction to the 3+ state is necessary prior to platinum extraction. Platinum is recovered via precipitation as ammonium hexachloro palatinate $[(NH_4)_2(PtCl_6)]$.

Iridium is reoxidized to the 4+ state, $IrCl_6^{2-}$, and is extracted by SX with tri-n-octyl amine (27). The extraction is carried out from concentrated HCl feed in order to ensure selectivity over rhodium. Nevertheless, some rhodium is co-extracted in a form which is not easily removable by scrubbing. Amongst the base metals, copper and lead are also co-extracted.

In order to increase iridium extraction, oxidizing conditions are used to suppress to reduction of Ir(IV) by the extractant. Ir(IV) is then stripped by reduction to Ir(III). The repeated cycling between oxidizing and reducing conditions leads to the rapid degradation of the amine.

To improve the solvent extraction separation of Ir(IV) a new extractant has been developed by Grant (27,28) and most likely has been now introduced in the refining circuit in the place of the trialkylamine . The new extractant an α mono N-substituted amide, has been reported to be highly selective for $IrCl_4^{2-}$ with a separation factor of $> 10^5$ against Rh(III).

The amide is diluted in an aliphatic diluent (Escaid 110) and a small quantity of TBP is added as phase modifier. The choice of diluent is important. Usually, an aromatic diluent (Solvesso 150) is used when ion-pair is formed in the organic phase since it increases the solubility of the extracted species. However, it was found (28) that some components of Solvesso 150 were easily oxidized and tended to reduce Ir(IV) to Ir(III) thus interfering with its extraction. Iridium is stripped from the amide extractant with 0.1M HCl. The purity of the iridium sponge is better than 99.84% with an overall yield better than 98%. In addition to the introduction of a new extractant for iridium some other changes (25) have been made to the earlier MRR flowsheet reported by Flett (5). Thus, the recuperation of Ru and Os via distillation is now performed after the extraction of platinum. Also, it appears that ion exchange chromatography is not used any more as originally thought to recover ruthenium.

2.2.4 The Lonrho Refinery

MINTEK, formerly NIM: The National Institute for Metallurgy, in South Africa has also developed a process for PGM recovery based on SX (1, 29-38). The original pilot tests were carried out in the Lonrho refinery at Brakpan in South Africa. It is obvious that since the 70s the original flowsheet developed by Edwards (29) has experienced several modifications since these have been discussed by Flett (5) and others (4,6).

The MINTEK flowsheet is the most complex one. The major changes made over the years are, (i) the selective leaching of base metals has been abandoned in favour of the total leach route, (ii) silver and gold were initially co-precipitated and then separated by selective recovery of gold with MIBK. Now, gold is believed to be recovered via reductive precipitation with SO_2 (33) or via solvent extraction by isodecanol, and (iii) platinum and palladium are no longer co-extracted. The most recent flowsheet of the MINTEK process is presented in Figure 2.4 (18).

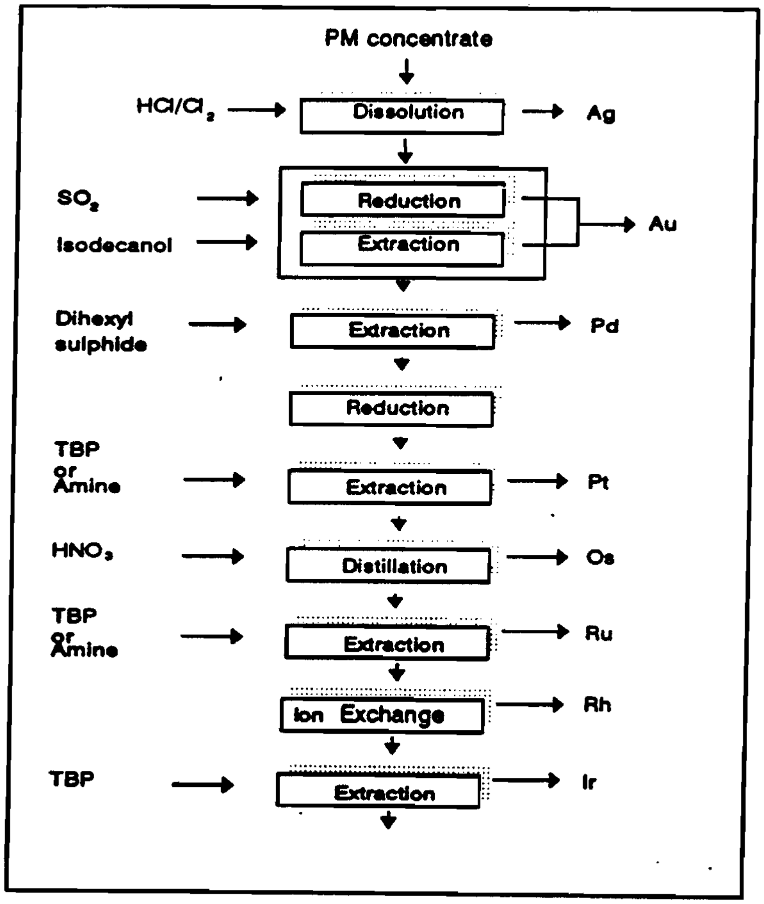

Figure 2.4 The Lornho refining flowsheet for the separation and recovery of PGM (18).

In the past, both palladium and platinum were co-extracted from the gold-free feed by an amine type extractant. More precisely an acetic acid derivative of the commercially available extractant; Amberlite LA-2 manufactured by Rohm and Haas was used. Then, both metals were stripped by HCl and palladium was subsequently and selectively re-extracted by di-n-hexyl sulphide rather than with the octyl analogue. The loaded organic was finally stripped by ammonia and further refined as in the INCO process. The purity of the palladium produced in this way ranged from 99.96 to 99.99%. Now the acetic acid derivative is not used any more but instead di-n-hexyl sulphide (34) is used to selectively extract palladium.

Prior to platinum extraction, the addition of formic acid to the feed solution allows the reduction of ruthenium and iridium to their 3+ states. Then platinum is extracted selectively by an amine or TBP (30,34). Following this, nitric acid is added to the feed. This leads to the formation of the stable complex $[Ru(NO)Cl_5]^{2-}$ allowing selective distillation of osmium (30,33). The ruthenium is then recovered via SX by a tertiary amine according to the following reaction

$$RuCl_6^{3-} + 3[R_3NH^+Cl^-]_{org} \rightleftarrows [(R_3NH^+)_3RuCl_6^{3-}]_{org} + 3Cl^- \qquad (2.8)$$

or by TBP . An aqueous solution of sodium hydroxide (10%) is used to strip ruthenium. The amine complex is reconverted to the hydrochloric form, with HCl, before recycling back to the extraction stage.

The iridium is then extracted via ion-exchange. The resin used is a quaternary ammonium salt, Amberlite IRA 400. Two scrubbing stages with concentrated and weak HCl solution allowed the removal of any entrained rhodium and co-extracted base metals respectively. A saturated aqueous solution of sulphur dioxide is then passed through the ion-exchange column. This achieves the reduction of Ir(IV) to Ir(III) which allows for its conversion to a highly charged mixed chloro-sulphito complex $[IrCl_4(SO_3)_2]^{5-}$ which is easily eluted by HCl. Although the ion-exchange process gives high selectivity with respect to base metals, the separation from rhodium is not as efficient as with solvent extraction. The eluate is therefore boiled to eliminate sulphur dioxide and then oxidized to convert the iridium back to $IrCl_6^{2-}$. This solution is further purified via SX by TBP. Finally iridium is precipitated as ammonium hexachloroiridate(IV) and can be calcined to produce iridium sponge.

The conversion of rhodium to an amine complex is also a well established procedure (30). The reaction of rhodium with an aqueous solution of ammonia in the presence of a catalyst such as ethanol or formaldehyde leads to the formation of the sparingly soluble Claus' salt, $[Rh(NH_3)_5Cl]Cl_2$. Simultaneously the base metals precipitate as hydroxides. The Claus' salt is very stable. Therefore, re-acidification with HCl dissolves the base metal hydroxides selectively which leads to purification of the salt. Whilst the separation from base metals is good, the precipitation of the Claus's Salt is not particularly selective over precious metals and the recrystallisation of this salt is not very effective either due to its low solubility. An early improvement involved warming the salt to 100°C with concentrated sulphuric acid to eliminate hydrogen chloride and to form the sulphate complex $[Rh(NH_3)_5Cl]SO_4$. This salt has a higher solubility and can therefore be easily recrystallised. It must then be converted back to the Claus's Salt via precipitation from a hot saturated solution with ammonium chloride prior to calcination to avoid the formation of the rhodium sulphate complex.

In the seventies MINTEK developed an alternative route to the purification of rhodium via the amine complex (35). According to this method the Claus's Salt is redissolved in a solution of sodium hydroxide as the complex $[Rh(NH_3)_5(OH)]^{2+}$, and the base metal hydroxides are filtered off. A solution of sodium nitrate is then added which leads to the formation of a soluble nitrito complex such as $[Rh(NH_3)_5NO_2]^{2+}$. The latter is precipitated as $[Rh(NH_3)_5NO_2](NO_3)_2$ by the addition of nitric acid. This procedure is claimed to be very selective over other precious metals. Furthermore the solubility of this salt increases rapidly with temperature and consequently it can be recrystallized quantitatively. However since the nitrate salt is potentially explosive, it must be converted back to the Claus's Salt before calcination and reduction to the metal. With this procedure the overall loss of rhodium is about 10%.

2.3 Other Reported Recovery Schemes

According to Harris (6), MINTEK and Degussa have conducted a very complete investigation of the solvent extraction of Pd(II) with di-n-hexyl sulphide and it is likely that Degussa is now using this process in their plant in Germany. Degussa (36) has also patented a new substituted thiourea which is used as a bulk precipitating agent for the precious metals, thus producing a clean precious metal concentrate for subsequent processing.

Johnson Matthey (37) has reported a new separation scheme, wherein, fluorination of precious metals is practised. With this method the precious metal fluorides can be distilled allowing the separation of palladium from other precious metals since it does not form such volatile fluoride salts. Dhara (38) from PGP Industries in USA, has proposed a total refining scheme based on the use of amines. Here the major inconvenience to such a process can be the various stripping agents needed to recover the extracted precious metals (39). Also, it is known that the stripping of loaded amines can be very difficult and kinetically slow.

2.4 8-Hydroxyquinoline Derivatives as Extractants for Precious Metals

Previous collaborative work between McGill University and CANMET

(Canada Centre for Mineral and Energy Technology) identified alkylated derivatives of 8-hydroxyquinoline to have very good extractive properties for precious metals. Thus in 1984 Pouskouleli and Demopoulos (40) reported studies on the co-extraction of Au(III), Pt(IV) and Pd(II) with Kelex 100 from chloride solutions. Co-extraction of Pt(IV) and Pd(II) with 8-HQ derivatives was affected via the following reactions:

(i) protonation of the extractant

$$HQ_{org} + HCl \rightleftarrows [H_2Q^+Cl^-]_{org} \tag{2.9}$$

(ii) anion exchange reaction of $PtCl_6^{2-}$

$$PtCl_6^{2-} + 2[H_2Q^+Cl^-]_{org} \rightleftarrows [PtCl_6^{2-}(H_2Q^+)_2]_{org} + 2Cl^- \tag{2.10}$$

(iii) chelate extraction of $PdCl_4^{2-}$

$$PdCl_4^{2-} + 2HQ_{org} \rightleftarrows PdQ_{2org} + 2H^+ + 4Cl^- \tag{2.11}$$

An important observation of this early work was the finding that an aromatic diluent (Solvesso 150) was essential in ensuring the solubility of the extracted Pt(IV) complex.

Later on, (41) the use of Lix 26 instead of Kelex 100 was proposed as the favourite reagent since it was found to exhibit higher solubility for Pt(IV) than Kelex 100.

The McGill-CANMET solvent extraction system basically involves (41) co-extraction of Pt(IV)/Pd(II) from gold-free chloride solutions followed by differential stripping with water (at controlled $pH > 1.5$) to recover Pt(IV) and strong (4-8M) HCl solution to recover Pd(II). Pilot-plant tests conducted at CANMET (42) confirmed the validity of the proposed new solvent extraction flowsheet. Patents covering the use of 8-HQ derivatives (Kelex 100) (43) and Lix 26 (44) for co-extraction of Pt(IV)/Pd(II) and differential stripping were granted in 1987.

Pouskouleli and Demopoulos (40) have also investigated the possibility of direct recovery of various precious metals by the integration of solvent extraction and hydrogen reduction. The above concept was introduced and investigated earlier for the production of some base metals (45,46). This method employs hydrogen reduction for direct recovery of gold, platinum and palladium via bulk co-extraction of PGM into the organic phase and stepwise precipitation of each metal in a powder form. Hydrogen was used as the reducing agent while Kelex 100 was used as extractant. The latter was found to give fast kinetics for Au(III), Pt(IV) and Pd(II) extraction from chloride solution. Pt(IV) was stripped selectively with hot water (60-80°C) and was recovered by hydrogen reduction of the aqueous strip solution at 60°C. Finally, Pd(II) recovery was effected directly from the organic phase by hydrogen reduction at 125-150°C. Further studies on precipitation of gold and palladium directly from the loaded organic phase were conducted in 1986 (47). According to these studies gold was found to be extracted as $H_2L^+AuCl_4^-{}_{org}$ and gold extraction was exothermic. Isodecanol was also found to be a weak gold extractant. However, its extracting power became significant only at acidities above 200g/L. A highly innovative feature of this work was the precipitation of gold by "hydrolytic stripping", i.e. contact between gold-loaded organic with water at elevated temperature (>20°C). Precipitation of gold was found to occur via a redox reaction which involved partial oxidation of the phenolic group of the 8-HQ extractant to a ketone and that of the alcoholic function of isodecanol (phase modifier) to the corresponding aldehyde. Moreover, this study clearly showed that direct recovery of palladium by hydrogen reduction was not practically feasible since this technique led to extensive degradation of both Lix 26 and Kelex 100. Instead, conventional stripping with concentrated HCl solution was recommended However, the recovery of platinum and palladium by hydrogen reduction of the aqueous strip solutions was quite satisfactory (48). Both metals could be readily precipitated at low temperature and low hydrogen over-pressure.

In the early piloting studies (42) it was found that the Pt(IV) loaded in the organic phase undergoes aging (>1 week storage) resulting in complex transformation. The latter presumably involved the slow transformation of the initially formed ion-pair between platinum and the extractant into a chelate complex which could no longer be stripped by water. Later a tentative mechanism (49) was proposed to explain the aging phenomenon. According to this mechanism, the redox reaction involved solely the metal ion and the extractant forming the extracted species. Besides, this type of intra molecular reaction did not involve atmospheric oxygen and thus differed completely from previous redox reactions which have been reported in metal solvent extraction. The following reaction has been postulated to explain the aging process.

$$[(H_2Q^+)_2PtCl_6^{2-} \cdot 2H_2Q^+Cl^-]_{org} \rightarrow PtQ_{2org} + [Q\text{-}Q]_{org} + 8H^+ + 8Cl^- \qquad (2.12)$$

Here, Pt(IV) is assumed to oxidize two molecules of Lix 26 (HQ) to form the corresponding dimer Q-Q while simultaneously the reduced Pt(II) species, $PtCl_4^{2-}$, being a more labile complex than $PtCl_6^{2-}$, undergoes a ligand exchange reaction thus leading to the formation of a chelate PtQ_2. Finally, it was found that an excess modifier (isodecanol or tridecanol) had to be used (modifier/extractant >1) to ensure good phase separation during Pt(IV) stripping with water (41,50).

Later on, this novel SX technology jointly developed by CANMET and McGill University was adopted and applied to the separation and concentration of platinum from a gold and palladium-free chloride feed produced by Noranda (50).

Finally, very recently, Demopoulos and researchers from the German Chemical company Schering AG have synthesized and tested a novel 8-HQ derivative (TN 1911) which appeared to outperform the presently other available commercial analogues (i.e., Kelex 100 and Lix 26) (51). In contrast to all other reagents used in the past, TN 1911 has been specifically designed for PGM separation. From a preliminary experimental assessment the new extractant appeared to offer the following advantages: fast kinetics, very good metal loading capacity and high separation factor ($S_f = D_{Pt}/D_{Pd} > 10^4$). The results have shown that Pt(IV) and Pd(II) were extracted via the same mechanism as with Kelex 100 and Lix 26. Co-extraction isotherms have shown that the relative metal loading capacity of each metal might depend on contact time. Thus longer contact time favoured the extraction of Pd(II) while short contacts favoured the extraction of Pt(IV). Following the very favourable extraction and stripping behaviour of TN 1911 vis-a-vis Pt(IV) /Pd(II) separation a comprehensive research program was launched to study the relevant chemistry of this system and to optimize various process parameters. As part of this program, Aprahamian (52) studied the behaviour of impurities during SX of Pt(IV)/Pd(II) with TN 1911 and identified several alternative scrubbing procedures for their control. In the meantime, Harris et al. (53) patented and piloted a flowsheet for Pt(IV)/Pd(II) separation with TN 1911 where following extraction, scrubbing with an HCl solution (pH 0-0.5) was incorporated to remove co-extracted impurities, (mostly Cu) and stripping of Pt(IV) was effected with the aid of a buffer solution rather than with pH control mentioned in the McGill-CANMET alternative flowsheet (41).

At the same time, Schering AG synthesized new 8-HQ derivatives which were named: TN 2181, TN 2221 and TN 2336. These reagents are alkenyl or alkyl derivatives (addition of an R group at the 7-position) of the parent 8-HQ. However, all these derivatives have different spatial orientation (conformation) and the R group can be a saturated or an unsaturated chain of various lengths. It is the scope of this thesis to report on the extraction and stripping properties of these novel reagents vis-a-vis Pt(IV) and Pd(II).

2.5 Solvent Extraction of Metals with Kelex 100

Since this thesis focuses on the extraction chemistry of Pt(IV) and Pd(II) with 7-substituted 8-hydroxyquinoline derivatives it is useful to review briefly the literature of metal solvent extraction with the best known member of this family of extractants, Kelex 100. Kelex 100 is a 7-substituted alkyl or alkenyl derivative of 8-hydroxyquinoline. Its structure is shown in Figure 2.5 (54).

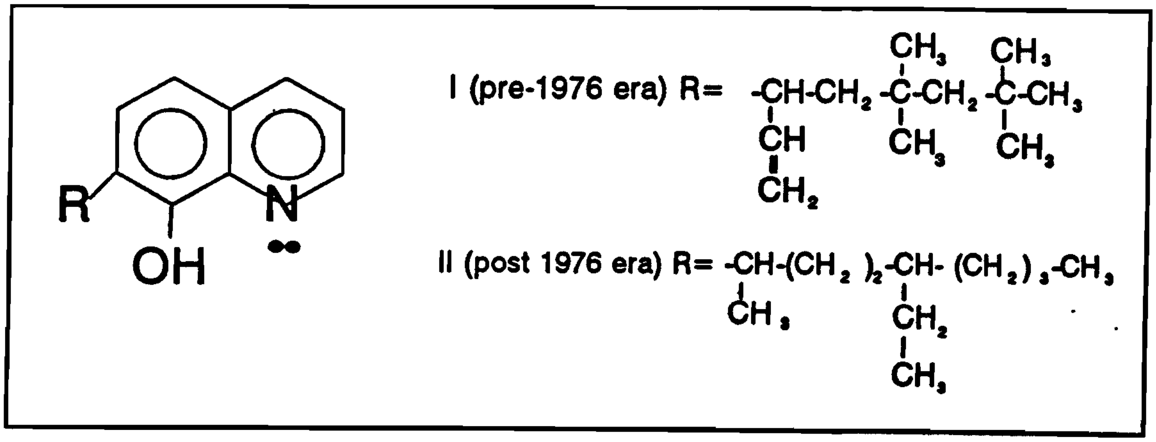

Figure 2.5 Detailed structure of Kelex 100 (54).

The possible usages of Kelex 100 have already been reviewed to some extent by Chengming (55) and, Bauer and Cote (56). The former reference described also some fundamental research conducted in China and the industrial applications of Kelex 100 in that country. The same author has also reported a series of seven other derivatives closely related to Kelex 100. In those derivatives, the position of the double bond and the branching of the side chain are different than those of Kelex 100. The Chinese analogue of Kelex 100 is known as N-601 (55). Kelex 100 can extract a large number of metals. The distributions of Fe, Ga, Cu, Ge, Ni, Co, Zn and Cd as a function of pH have been reported (56).

Initially, Kelex 100 had been developed specifically to compete with the hydroxyoxime group of extractants for copper extraction (57). The extraction of copper from sulphate media has been extensively studied. However, commercial application of Kelex 100 to the copper industry has never materialized due to two principal reasons: (i) poor selectivity over Fe(III) (58,59), and (ii) considerable acid extraction via protonation during stripping (60). Some of the studies on copper extraction include: the effect of diluent (61), equilibria and kinetics (62-65), comparison with Lix 65N (H_2SO_4 media) (62), mathematical model for distribution (66,67) and finally the effect of two phase modifiers namely nonyl phenol and decanol (68).

Cobalt extraction with Kelex 100 has also been reported (69-71). Nevertheless, it should be pointed out that Co(II) is readily oxidized during extraction to the cobaltic state (72,73). However, the oxidation rate can be significantly reduced by the use of additives (74). Oxidation to Co(III) is totally undesirable as it causes metal lock-up.

Lakshmanan and Lawson (75) have reported the extraction of Cd from aqueous sulphate or chloride solutions with Kelex 100 and Versatic 911 (a C_9-C_{11} tertiary monocarboxylic acid) dissolved in kerosene. An enhancement of extraction was observed when mixtures of both extractants were used. The separation of Zn and Cd has also been reported (76).

The use of 8-hydroxyquinoline for gallium recovery from aluminate alkaline solutions has been patented in France (77). The principles of the process have also been published (78). The commercial application of Kelex 100 for gallium recovery from Bayer aluminate liquor has been discussed by Flett (79). The extraction of gallium from nitrate media has also been reported (80,81). More recently some alternative to conventional solvent extraction techniques for the recovery of gallium have been published and amongst these are the usage of a resin impregnated with Kelex 100 (82) and, the use of ultrasound (83). The existence of a microemulsion in the solvent extraction system of gallium with Kelex 100 and Versatic acid has been demonstrated by Bauer et al. (84). Spectroscopic characterization of the extracted species formed between Kelex 100 and gallium has also been reported (85).

Kelex 100 has been selected for the extraction of Ge from H_2SO_4 media (86,87). The extraction involved the formation of an ion-pair. But, Lix 26 can be used in the place of Kelex 100 (88).

The extraction of lead with Kelex 100 has been reported to be slow (89). Very recently, Desantis and Distin (90) reported the recovery of lead by Kelex 100 from acetate solutions. Metallic lead was produced directly from the organic phase via hydrogen reduction.

Several aspects of the extraction of nickel by Kelex 100 have also been studied to some extent (91-94). A mixture of Kelex 100 and 8-hydroxyquinoline or 1,10-phenanthroline has been used to extract some lanthanides (95). Finally, the extraction of the following metals has also been reported: molybdenum (96), iron (97-100), the uranyl ion (101), zinc (102), lanthanum and cerium (103).

2.6 References

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Chapter 3

Characterization of 7-Substituted 8-Hydroxyquinoline Derivatives, and HCl and Water Extraction[1]

3.1 Abstract

Extensive characterization (IR, UV,^{1}H-NMR and GC-MS) of new, non commercially available 7-substituted-8-hydroxyquinoline derivatives [8-HQ][2], labeled TN 1911, TN 2181, TN 2221 and TN 2336, manufactured by Schering Berlin AG., (Germany) is reported here. [In addition to these reagents, Kelex 100 and Lix 26 the commercially available 8-HQ were also used in the present study as references material]. GC-MS allowed for the identification of isomers present in TN 1911 and Lix 26 (Henkel) extractants. Purity, molecular weight and

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[2] [ ] are used to denote material that was not published in the original paper. These short additions are made to better integrate the published paper in a coherent thesis format.

molarity of the active substance in the "as received" extractants, are also reported. Finally, hydrochloric acid and the accompanied water extraction performance of Kelex 100, TN 1911 and Lix 26 as well as the occurrence of protonated extractant in the organic phase are also discussed.

3.2 Introduction

The growing demand for platinum-group metals (PGM) for several applications, the need for modern and clean processes and the increasing volume of low grade material for secondary PGM recovery have a direct impact on the industrial practice of recovering and refining of precious metals at the present time. Traditionally, recovery of PGM was achieved through an extensive series of precipitation-dissolution steps followed by calcination to produce pure metal sponge (1). Nowadays, solvent extraction (SX) proves to be the most suitable and powerful separation technique for PGM recovery and refining.

At McGill University, extensive research on the extraction of PGM with 8-hydroxyquinoline derivatives (8-HQ) is underway. In the early phase of this research project, commercially available alkylated-8-HQ derivatives namely Kelex 100, a proprietary product of Sherex Chemical Co., Dublin, Ohio, and Lix 26 made by Henkel Corporation, Arizona, were investigated (2-4). Presently, we are investigating PGM extraction with new, non-commercially available 8-HQ derivatives specially synthesized for PGM separation and recovery by Schering Berlin AG., Germany. These experimental reagents are labeled: TN 1911, TN 2181, TN 2221 and TN 2336. These extractants are mono-substituted alkyl or alkenyl derivatives of the parent 8-HQ. Today, at least one of these extractants (TN 1911) appears to outperform both Kelex 100 and Lix 26 (5). All these reagents, which, in fact are 7-substituted-8-HQ operate via the so-called branch extraction route that involves Pt(IV) and Pd(II) coextraction followed by selective stripping (5).

In the present investigation, the above mentioned 8-HQ extractants are characterized and their extraction performance is reported in terms of HCl and water extraction from concentrated chloride media. In subsequent papers [chapters 4, 5 and 6], the extraction chemistry of Pt(IV) and Pd(II) with these reagents will be described.

3.3 Experimental

Kelex 100 supplied by Sherex Chemical Company, Dublin, Ohio, was a typical post-1976 product. Lix 26 was supplied by Henkel Corporation, Tucson, Arizona, and all TN extractants and Kelex 100S, a higher purity version of Kelex 100, were supplied by Shering Berlin AG.,Bergkamen, Germany.

Purification of the "as received" extractants consisted of contacting a 0.30M solution of each extractant with an equal volume of 1.42M HCl for 3 consecutive times. This was followed by several washings with equal volumes of water until no chloride was detected in the wash water.

Before GC-MS was performed, the purified Lix 26 and TN 1911 samples were silylated with bi-silytrifluoroacetamide (BSTFA-Piece Chemical Company, Rockford, Illinois). The infrared spectra were recorded in the range 4000-400cm^{-1} using a Perkin-Elmer model 1330 spectrophotometer and a NaCl cell. UV studies were carried out with a Varian Cary 13 UV-visible-spectrophotometer and $CHCl_3$ spectrograde was used as solvent. ^{1}H-NMR spectra were recorded in the range -10 to 10 ppm using a Varian Gemini 200 MHz. C_6D_6 and trimethylsilane were used as diluent and internal reference solutions respectively.

Hydrochloric acid titrations in aqueous solutions were performed with an automatic titrator at a pre-selected end-point set at pH 7.00. Analytical grade 0.100M NaOH has been used as titrant. [HCl content of the organic phase has been determined by difference between the acidity in the feed and raffinate respectively.] Finally, water content in the organic phase was determined by Karl Fisher titration.

3.4 Results and Discussion

3.4.1 Reagents Structure

Table 3.1 shows the principal features of several 8-HQ derivatives. Figure 3.1 shows the detailed structure of one possible unsaturated isomer present in TN 1911. Here, the vinyl group is branched to the alpha carbon of the main chain. It is the nature and the orientation (conformation) of the side chain, R, that characterizes the various extractants. For example, TN 1911 and TN 2181 have similar unsaturated R group (C_{11}-C_{13}), but with different conformations (Table 3.1). In the former, the side chain is oriented towards the two bonding sites, the phenol (C-OH) and the heterocyclic (N) which causes a high steric hindrance. In [Fig. 3.1, the rotation of the vinyl group causes the steric hindrance at the bonding sites, the steric hindrance caused by this special conformation of the main chain, as described above, is shown in Fig. 3.1.] The position and number of double bonds in the side chain of TN 1911, as well as for the other unsaturated TN extractants is not known with absolute precision. Information about TN's extractants conformation has been provided by the manufacturer.

The addition of an R chain to the parent molecule (8-HQ) plays several roles. It increases the hydrophobicity of the extractant and improves metal selectivity during the extraction stage. It is well known that 8-hydroxyquinoline is significantly soluble in water which leads to extensive loss of extractant to the aqueous phase.

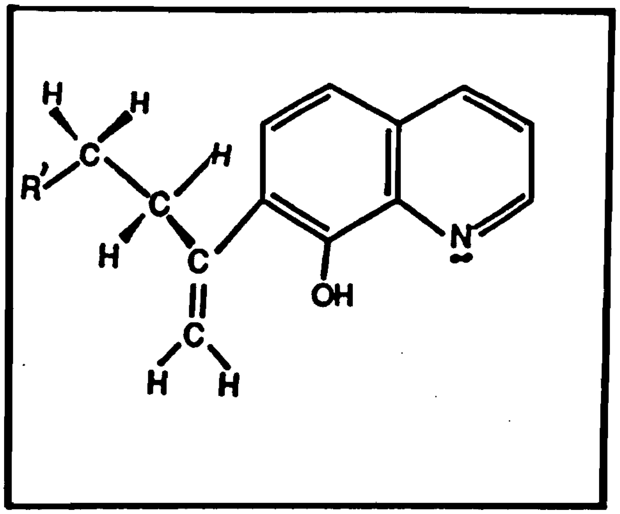

Figure 3.1 Detailed structure of one possible isomer of the active isomer present in TN 1911.

Table 3.1 Some features of 8-HQ derivatives

	R Group				Steric Hindrance	
Reagent	Sat	Unsat	# Carbon	Isomer	Low	High
TN 1911		X	10-13	Y		X
TN 2181		X	10-13	?	X	
TN 2221	X		10-13	?		X
TN 2336	X		10-13	?	X	
Kelex 100	X		11	N	(**)	
Kelex 100S	X		11	N	(**)	
Lix 26		X	11-14	Y		X

(*) Sat, unsat mean saturated and unsaturated respectively
(**) Medium Steric Hindrance

3.4.2 Composition

Commercial extractants are often mixtures of structural and positional isomers as well as by-products. Ashbrook (6,7) has described the isolation and the characterization of the active component of Kelex 100 and Kelex 120, two proprietary metal extractants which were produced by Ashland Chemical Co. (now WITCO Co.). Before 1976, the main active component of Kelex 100 was 7-(1-vinyl-3,3,5,5-tetramethylhexyl)-8-hydroxyquinoline. Ashbrook, however, does not report the full list of components present in that extractant but he does report that Kelex 100, at that time, consisted of about 77.7% of the active component and 3.7% 8-hydroxyquinoline. The remainder was an unknown viscous fluorescent material due likely to decomposition during the synthesis of Kelex 100. In 1976, the manufacturing process of Kelex 100 was changed so that the active component now is 7-(4-ethyl-1-methyloctyl)-8-hydroxyquinoline. The new synthesis route was patented in 1977 by Richards et al. (8). Demopoulos and Distin (9) have described the composition of Kelex 100 (post-1976) by gas chromatography (GC) and mass spectroscopy (MS). The following composition was found: 7-(4-ethyl-1-methyl octyl)-8-hydroxyquinoline, the active component, 82%, 7-(2-ethylhexyl)-8-quinolinol 1%, 7-(4-ethyl-1-methyloctyl-1-ene) 8-quinolinol 0.5%, 9-ethyl furoquinoline 8%, 8-methyl-9-(2-ethylhexyl) furoquinoline 4.5% and 8-methyl-9-(2-ethylhexyl) dihydrogenated furoquinoline 0.5%.

Gareil et al. (10) have analyzed post-1976 Kelex 100 by liquid chromatography (LC) and MS and they outlined the new synthesis route for Kelex 100 patented by Richards. Most of the compounds identified by Demopoulos and Distin (9) were confirmed, but in addition, a ketone probably 3-octyl dodecyl methyl ketone, and two alcohols were identified. Conversely, the major impurity previously identified (9): 9-ethyl furoquinoline, was not found. This is most likely due to the new improved synthesis route.

GC-MS spectroscopy of TN 1911 and Lix 26, the data are shown in Table 3.2, confirmed that both extractants are monosubstituted at the 7 position and are very similar. Lix 26 has 2 series of homologues, an R side chain with various number of carbon atoms, named here series 1 and series 2. Series 1 was more abundant than series 2 and, also, in series 1 and 2 the side chain has one and two unsaturations respectively. In the case where two unsaturations are present, one might be branched to the main chain as shown in Fig. 3.1, while the other is randomly located in the main chain. For TN 1911, only a series of mono-unsaturated isomers have been observed. For one possible isomer, the double bond is located at the alpha carbon with respect to the fused ring system as shown in Fig. 3.1.

In the present work, emphasis has been placed on characterizing the various isomers present in the extractants, whereas, previous studies (9,10) focused on by-product or impurities identification.

Table 3.2 Comparative GC-MS analysis of the relative abundance of the major compounds of series 1 of Lix 26 and TN 1911

m/e(*)	269	283	297	311	325	339
R Group	C_9H_{17}	$C_{10}H_{19}$	$C_{11}H_{22}$	$C_{12}H_{23}$	$C_{13}H_{25}$	$C_{14}H_{27}$
TN 1911	0.8	11.3	39.9	42.8	5.0	N/D(**)
Lix 26	N/D	N/D	27.2	64.7	7.0	1.0

(*) m/e: mass/charge ratio, (**) N/D: not detected.

3.4.3 UV-Visible Spectroscopy

UV spectra of several 8-HQ derivatives in $CHCl_3$ have been recorded, data are presented in Table 3.3 and a typical spectrum of TN 1911 is presented in Fig. 3.2. The electronic transition which accounts for the position of the absorption band is $\pi \rightarrow \pi^*$.

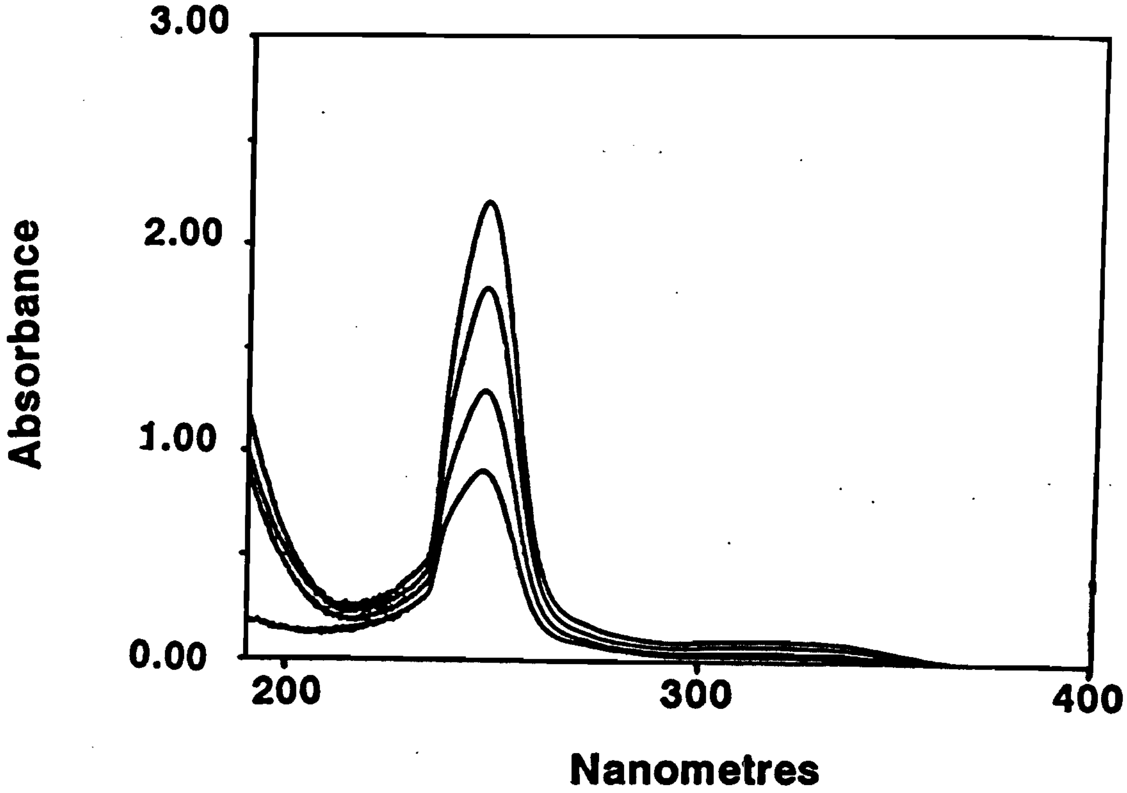

Figure 3.2 Ultra-violet spectra of TN 1911. ($[TN\ 1911]_{org}=1.73\times10^{-5}$, 2.61×10^{-5}, 3.48×10^{-5} and 4.35×10^{-5}M) in $CHCl_3$.

Previous UV data reported by Ashbrook (7) show that Kelex 100 (pre-1976) exhibits absorption maxima at 247, 267, 313 and 303 nm in absolute alcohol. The same author has also reported that the log of absorptivity coefficient (ϵ) at 247.1 nm was 4.70. For Kelex 100 (post-1976) in $CHCl_3$, and all 8-HQ derivatives studied here, there is only one broad absorption band with a maximum wavelength located at 248.1 nm.

Table 3.3 UV-Visible characterization of 8-HQ derivatives in $CHCl_3$

Reagent	λ_{max} (nm)	log ϵ	Linearity [ ] × 10^{-5} M
TN 1911	248.8	4.71	0.8-7
TN 2336	248.8	4.68	0.8-7
Kelex 100	248.1	4.65	0.8-7
Kelex 100S	248.3	4.67	0.8-8
Lix 26	240.0	4.60	0.8-8

3.4.4 Infrared Spectroscopy

The IR spectrum of TN 1911 is shown in Fig. 3.3. The assignments of the observed frequencies are shown in Table 3.4. Also, for comparison purposes, the spectrum of the active substance in Kelex 100 (post-1976) has been recorded. A good agreement between the frequencies reported by Marchon et al. (11) and those observed in our spectra was found. In general, the spectra of Kelex 100 and TN 1911 were similar. Frequencies of the latter were shifted about 10-15 cm^{-1} to lower wavenumber with respect to the former. Demopoulos and Distin (9) have previously reported the spectrum of Kelex 100 and also made assignments for the active substance of Kelex 100 (post-1976). More recently, Marchon et al. (11) have published revised IR and Raman data for pure 8-HQ and purified Kelex 100. New assignments for O-H in plane bending, C-O stretching and ring breathing modes are suggested.

The major differences between these two studies lies in the assignments of the bands located at 1279 and 724 cm^{-1}. Marchon and coworkers have assigned the first one to the O-H in plane bending mode, whereas Demopoulos and Distin, to the C-N stretching mode. The band observed at 724 cm^{-1} was ascribed to the ring breathing mode by Marchon et al. and to a C-N bending mode by Demopoulos and

Distin. When taking into account Raman spectroscopic evidence provided by Marchon et al., it seems that the assignments made by these authors are justifiable. However, they did not report which absorption was related to the C-N stretching mode of the hetero-ring. The latter, according to Berg (12) should be observed in the region 1580-1600 cm^{-1}. This assignment was previously made for Kelex 100 (post-1976) (9), but Marchon et al. only reports a ring vibration at this frequency instead. For TN 1911, the band observed at 710 cm^{-1} does not have the appropriate shape and the intensity to be the ring breathing band. Also, the absence of absorption at 1330 cm^{-1} is not, at the moment, completely understood. Finally, no direct IR evidence to support the presence of an unsaturation (C=C) in the sidc chain of TN 1911 was found.

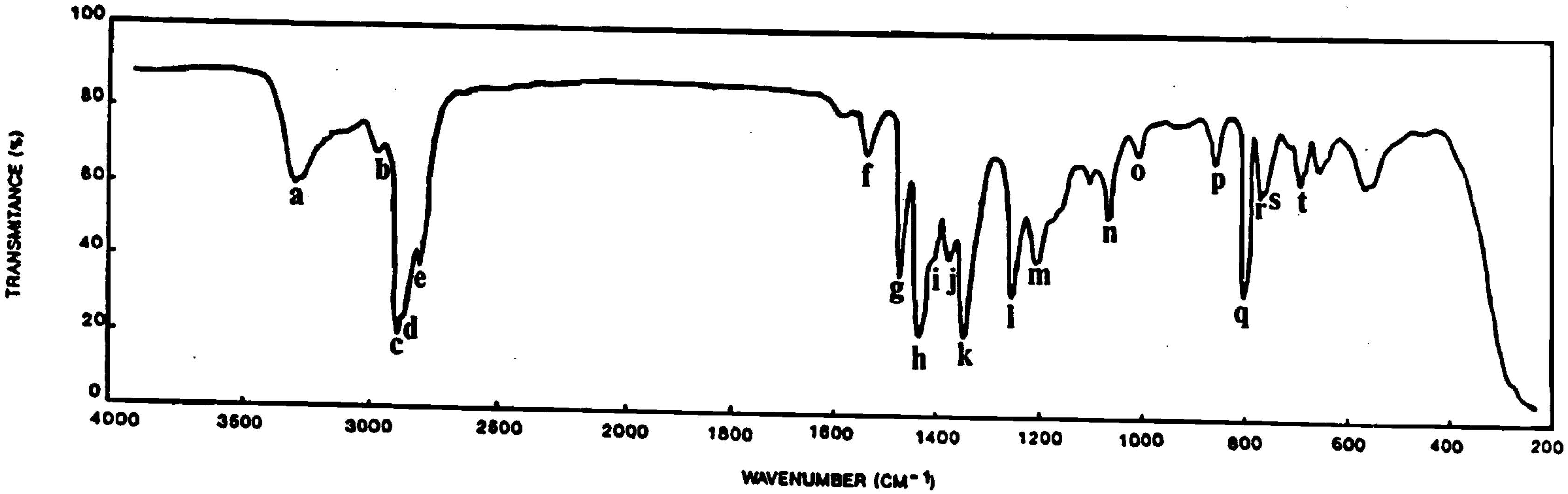

Figure 3.3 Infrared spectrum of TN 1911 as a film on a NaCl cell.

Table 3.4 Assignments of the main fundamental frequencies (cm $^{-1}$) of the acitve substance in TN 1911

Frequency (cm^{-1})	Band in Fig 3.	Assignments
3360	a	Stretching frequency of intra-molecular hydrogen bond O-H
3030	b	Aromatic C-H stretching
2940	c	Stretching modes of methyl and
2920	d	methylene groups
2840	e	
1560	f	C-N Ring vibration
1490	g	Ring vibration
1450	h	Ring vibration + bending mode of methyl and methylene groups
1425	i	Ring vibration
1395	j	Ring vibration
1360	k	Ring vibration + bending mode of methyl and methylene
1270	l	O-H in plane bending mode
1220	m	----
1080	n	C-O stretching
1030	o	Ring vibration
880	p	----
820	q	Out of plain ring C-H bending
790	r	Out of plain ring C-H bending
775	s	----
710	t	Ring breathing

3.4.5 Proton Nuclear Resonance

A study of Proton Nuclear Magnetic Resonance (^{1}H-NMR) of the "as received" TN 1911 and TN 2336, in deuterated benzene was performed (see Figs. 3.4 and 3.5). For TN 1911, signals located in the aliphatic and olifenic region are rather broad which confirms the presence of by-products as well as a mixture of structures, i.e. branched and normal aliphatic R chains and position isomers, i.e. olefinic protons located along the chain at different positions.

Chemical shifts related to methyl protons are located at about 1.0 ppm, whereas those related to methylene groups are located at 1.3, 1.5 and 1.7 ppm with respect to trimethylsilane. Also, the relative integration of the methyl and methylene signals suggest that TN 1911 is a mixture of normal and branched R groups. In addition to this, chemical shift related to either a CH group alpha to a ketone, or a $C=CH_2$ alpha to the aromatic ring was located at 2.1 ppm. The presence of alcohols could explain chemical shifts observed at 3.6, 3.8 and 3.9 ppm respecitvely.

Olefinic protons have been observed as a broad signal centered at 5.2 ppm. The aromatic protons were located at 6.7, 7.1, 7.5 and 8.4 ppm. The signal located at 6.7 ppm was ascribed to the proton in the para position with respect to the phenol group, and that at 8.4 ppm was most likely related to the proton in alpha of the nitrogen atom. Finally, the proton of the phenolic group had a chemical shift at 8.85 and 8.40 ppm. The first one is ascribed to 8-HQ, the parent molecule which is present as a by-product, whereas the second belongs to the active extractant. The presence of 8-HQ has been also reported by Ashbrook (7).

The same observations also applied to the spectra of TN 2336 except that no olefinic protons were observed. Ashbrook (8) had reported some ^{1}H-NMR data for Kelex 100 (pre-1976) in CCl_4 and these confirmed the structure of the active extractant that he reported earlier (6).

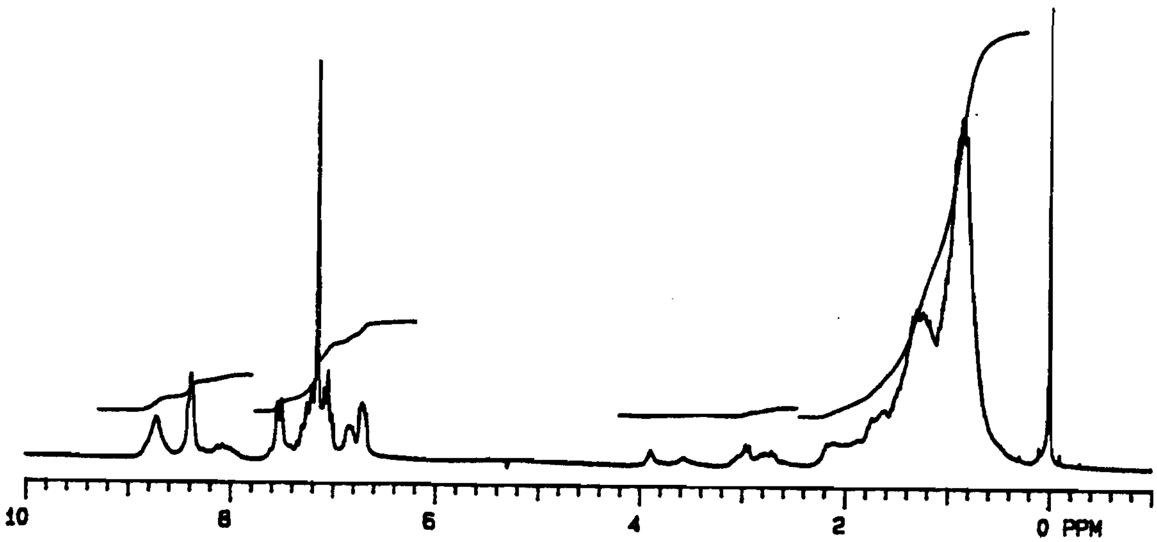

Figure 3.4 ^{1}H-RMN spectrum of TN 2336 in C_6D_6.

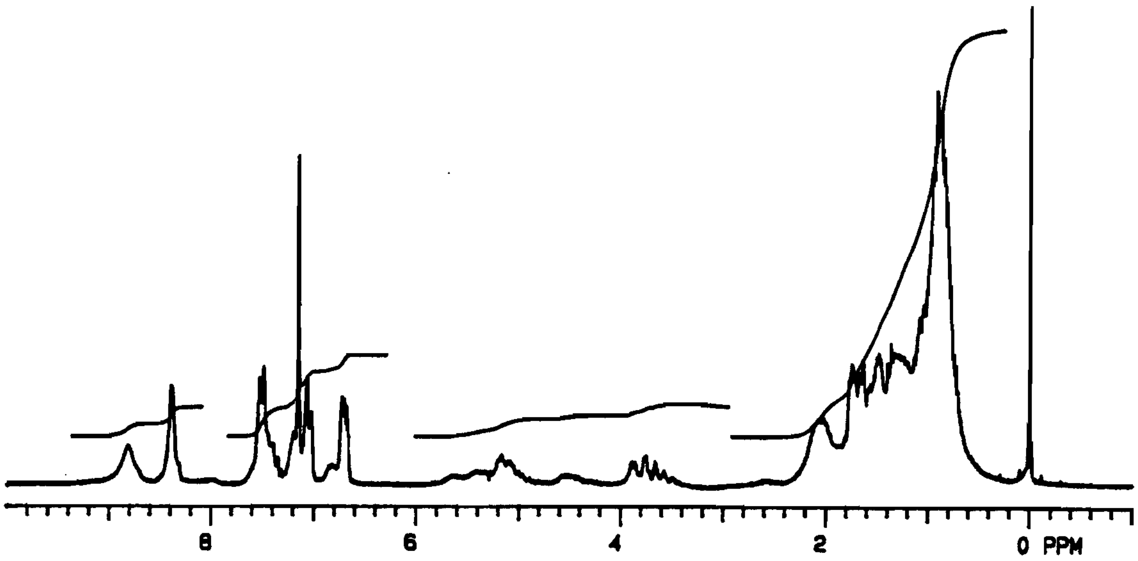

Figure 3.5 ^{1}H-RMN spectrum of TN 1991 in C_6D_6.

3.4.6 Purity and Molecular Weight

The purity of the "as received" extractants has been evaluated by two different methods. The first method is by copper loading (13) and the second one by titration with perchloric acid in a glacial acetic acid medium (14). The molarities of the "as received" extractants determined from both methods are reported in Table 3.5. The molecular weights of TN 1911 and Lix 26 were determined by GC-MS as well as from copper loading experiments. The molecular weight reported for these two extractants in Table 3.5 are the weight average molecular weight calculated from GC-MS data, where the relative abundance of each component has been taken into account. For the remaining extractants, the molecular weight was determined only by copper loading. Also, for TN 1911 and Lix 26 the values of the molecular weights determined from the latter method agree well with the weight average molecular weights calculated from the GC-MS data.

Molarities have been calculated from the stoichiometries of the copper extraction (13) and from neutralization (14) reactions respectively. The former was assumed to be, on a molar basis, 2:1 with respect to the amount of copper extracted and, therefore, the extracted species was CuL_2, where L represents the organic extractant. The latter was assumed to be equal to the number of moles of perchloric acid needed for reagent neutralization. The percent purity is defined as the ratio of the two molarities since copper extraction involves both bonding sites of the extractant, whereas neutralisation involves only the nitrogen atom. Finally, the molecular weight and purity reported by Freiser (15) for Kelex 100 and those reported in Table 3.5 are in good agreement. However, caution must be exercised when evaluating the effective concentration of the active extractant in solution. The difference in the molarity values determined by the two methods can be explained by the fact that most of the by-products identified in the "as received" extractant contained a nitrogen atom in the molecule (9). This leads to molarity overestimation via perchloric acid titration. However, by-products able to extract copper seem to be less abundant and, therefore, the molarity measured via copper extraction technique will be more accurate in determining the concentration of the major active derivatives of 8-HQ.

Table 3.5 Purity and molarities of 8-HQ derivatives

Reagent (Method)	Molarity (Acid)	Molarity (Cu loading)	Molecular Weight	% Purity
TN 1911	3.10	2.90	311	93
TN 2181	3.20	2.60	311	81
TN 2221	3.07	1.97	313	64
TN 2336	3.20	2.56	313	80
Lix 26	2.55	1.61	308	63
Kelex 100	3.12	2.43	299	78
Kelex 100S	3.18	2.80	299	88

[Finally, the long-term chemical stability of these extractant has been studied. The results have not however been published in the original article and are therefore presented in Appendix A (Figure A.1)].

3.4.7 Hydrochloric Acid Extraction by 8-HQ Derivatives

3.4.7.1 Solvesso 150 solution

All 8-HQ derivatives become protonated upon contact with HCl solutions. The organic reagent (HQ) extracts hydrochloric acid according to the following reaction:

$$HQ_{org} + HCl_{aq} \rightleftarrows [H_2Q^+Cl^-]_{org} \qquad (3.1)$$

This is due to the basic character of the nitrogen atom present in these extractants.

In Figure 3.6[3], the acid concentration in the organic phase, $[HCl]_{org}$, is plotted against the equilibrium acid concentration in the aqueous phase, [HCl].

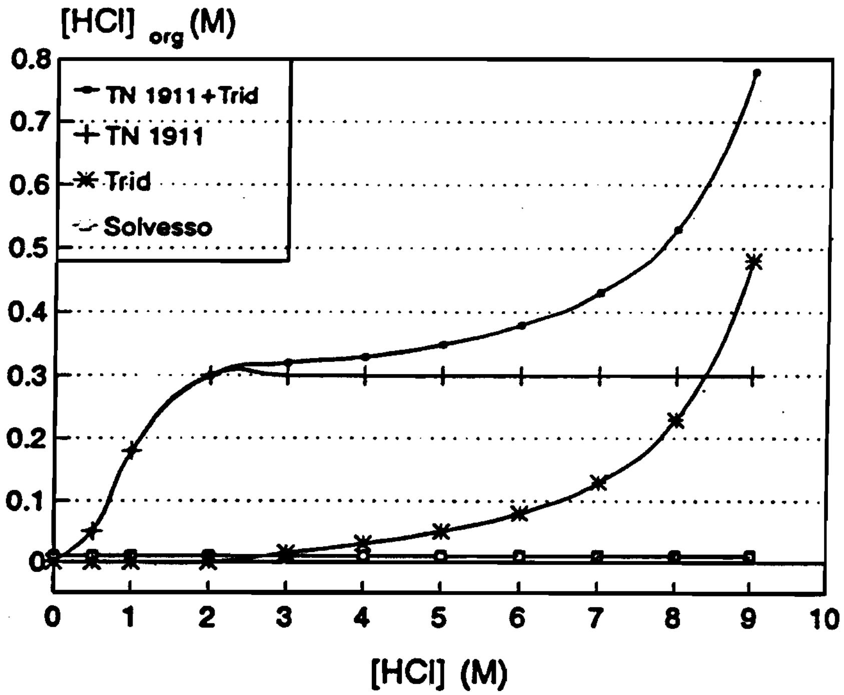

Figure 3.6 HCl distribution in (i) 0.30M TN 1911 + 1.0M Tridecanol, (ii) 0.3M TN 1911, (iii) 1.0M Tridecanol, and (iv) Solvesso 150.

This figure shows that the extent of HCl extraction depends on the solvent composition and since high MW alcohols like tridecanol are used as phase modifiers, the extraction of acid by the modifier itself has been considered as well. Solvesso 150 (97% aromatic content) was used as diluent. It can be clearly seen that tridecanol extracts measurable amounts of acid at [HCl] above 4.00M. This has an important effect on the overall process performance. Finally, the individual

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[3] The original figure (Figure 6) puslished in Solvent Extraction and Ion Exchange, 11(2), (1993) was in error as it had underestimated the amount of acid extracted by the modifier. This figure was corrected as an Appendix in Part 3 of the published series of papers (Solvent Extraction and Ion Exchange, 12(3), in press. The corrected Figure is shown here.

ability of TN 1911 to extract HCl was determined as the difference between the top and the bottom curve. These data also confirmed that the extractant becomes almost fully protonated at 2.00M HCl as it does in the corresponding chloroform system [Section 3.4.7.2]. From Figure 3.7[4], it is obvious that, at similar reagent concentration (0.30M), Lix 26 extracts more acid than TN 1911. Again, tridecanol and Solvesso 150 were used as modifier and diluent respectively. Also, as the acidity of the aqueous phase increases, the value of $[HCl]_{org}$ increases and approaches the initial extractant concentration which confirms the stoichoimetry of Eq. 3.1.

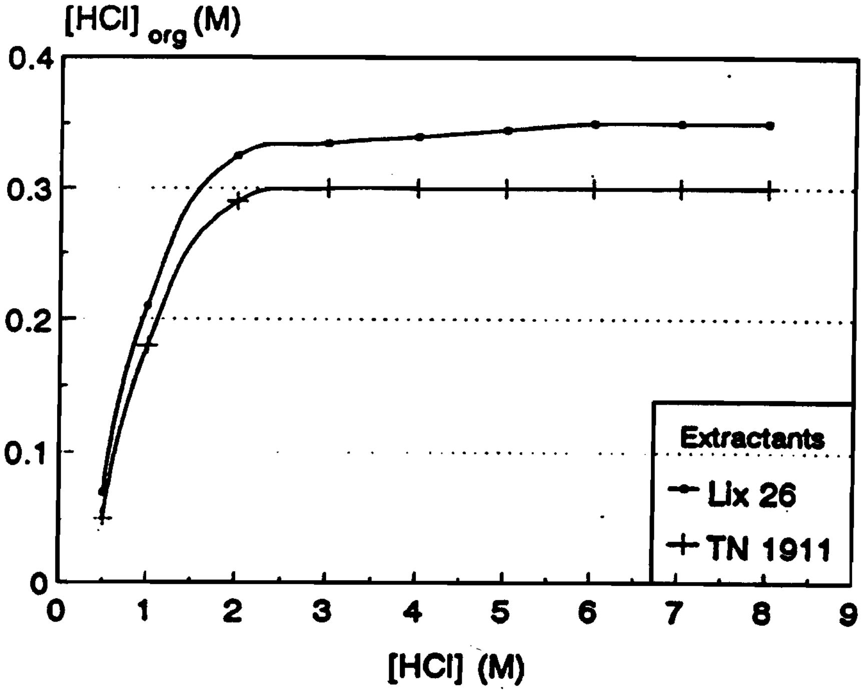

Figure 3.7 HCl distribution in 0.3M TN 1911 and 0.3M Lix 26 in Solvesso 150 solutions at 25°C.

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[4] The same correction was made here as per the footnote page 57

3.4.7.2 Chloroform solution.

Figure 3.8 shows the amount of acid extracted by chloroform solutions of TN 1911 at various equilibrium aqueous HCl concentration. Here, no tridecanol was added to those solutions and complete protonation can be seen to occur at [HCl] of about 2.0M.

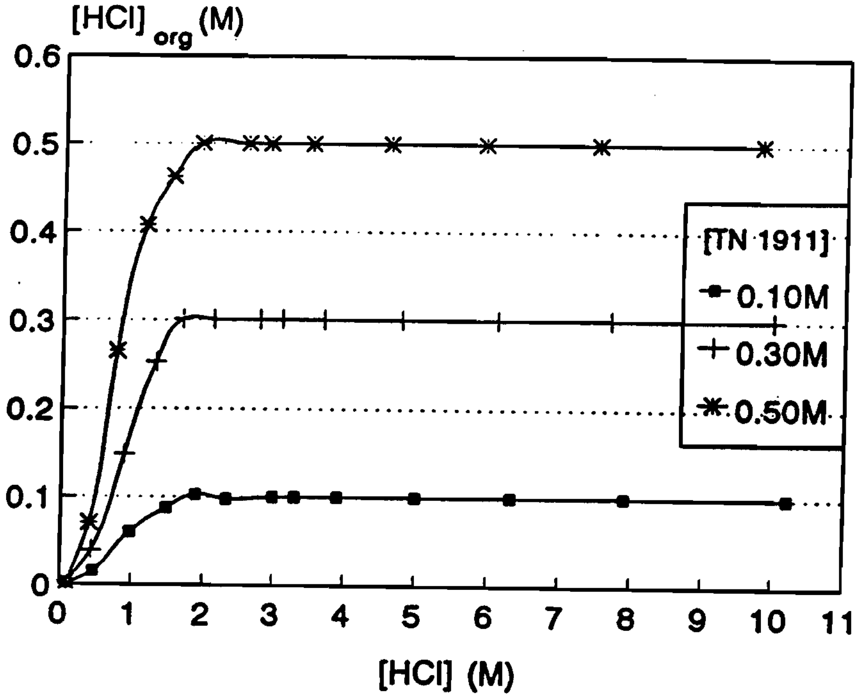

Figure 3.8 HCl distribution in TN 1911 in $CHCl_3$ solutions.

This level is similar to the corresponding Solvesso 150 system.

These results are significantly different from those reported earlier by Ma and Freiser (15) for chloroform solution of Kelex 100 (post-1976). These authors have reported that the ion-pair formed between Kelex 100 and HCl was present as a small fraction (about 4% in 2.00M HCl) of the neutral extractant in chloroform.

This discrepancy between Kelex 100 and TN 1911 to extract acid cannot be explained by structural differences between the two extractants since they both experience steric hindrance but only TN 1911 has an unsaturated side chain.

Upon contact of either a Solvesso 150 or a $CHCl_3$ solution of TN 1911 with aqueous HCl, the organic phase becomes yellow. The UV absorption band of chloroform solution of TN 1911 was consistent with the formation of an ion-pair between TN 1911 and HCl according to Eq. 3.1. A similar observation has been reported by Ma and Freiser (15). Also, when the acidity of the aqueous phase was increased a very broad peak was observed in the chloroform phase centered around 390 nm, whose absorbance was directly proportional to the increasing acidity.

The nature of the diluent does not influences the extraction of HCl. The higher dielectric constant of chloroform (16) with respect to that of Solvesso 150 could not be held responsible for this discrepancy.

In Figure 3.9, the extraction ratio of hydrochloric acid, Z, is defined as $[HCl]_{org}/[HQ]_{initial}$. The value of Z increases and reaches a maximum of one independently of [HQ] with increasing [HCl] which further confirms the stoichiometry of Eq. 3.1 in chloroform. A similar technique has been used to confirm the stoichiometry of HCl extraction with an amine (17).

A speciation diagram of the free, HQ, and protonated extractant, $H_2Q^+Cl^-$ in chloroform as a function of [HCl] is presented in Figure 3.10.

From Figs. 3.8, 3.11 and 3.12, the apparent equilibrium constant of HCl extraction reaction, K'_{eq}, (Eq. 1) was determined at 25 °C in either Solvesso 150 or chloroform solutions for the various extractants.

The reagent concentrations used for those determinations were 0.3, 0.5 and 0.7M in Solvesso 150; and those in $CHCl_3$ solution were 0.1, 0.3 and 0.5M respectively. All solutions were contacted with HCl solutions of concentrations betwen 0.2 to 0.8M. In Solvesso 150 solutions, tridecanol was added as twice the

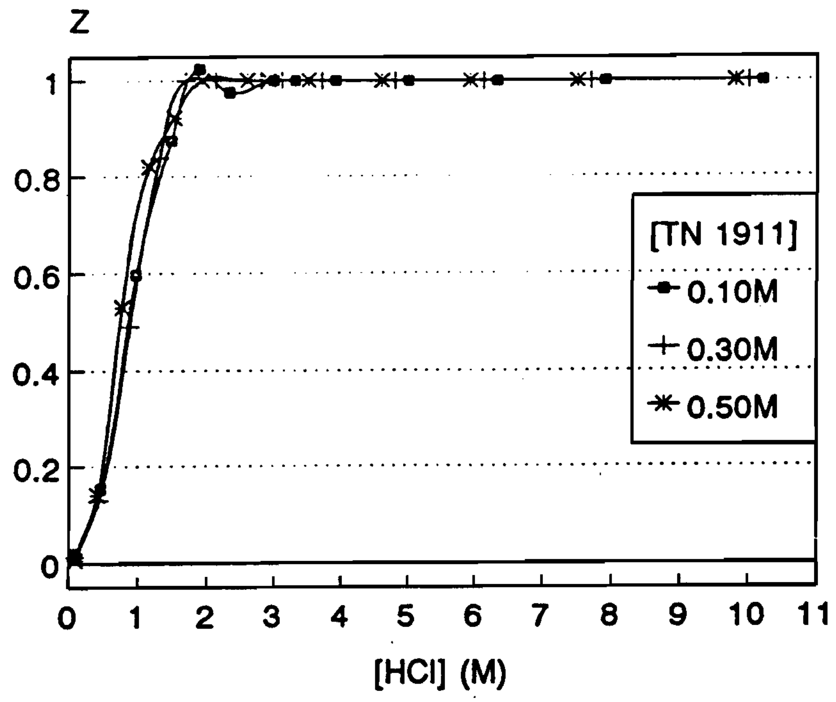

Figure 3.9 Relation between distribution ratio of hydrochloric acid, Z, and HCl concentration in the aqueous phase.

extractant mass, as phase modifier in order to improve phase separation. However, in chloroform, phase separation was such that no modifier was necessary.

Finally, the modifier's ability to extract HCl was taken into account in K'_{eq} evaluation.

All experimental data were first plotted as $[HCl]_{org}$ vs [HCl] at equilibrium. Then, linear regression allowed us to determine the [HCl] at a given $[HCl]_{org}$. The latter was fixed at 0.05M in order to fullfill the conditions usually used in slope analysis. Finally, plots of log D_{HCl} vs log $[reagent]_{free}$ gave a straight line of slope 1 and the intercept corresponding at log K'_{eq}. The slope value further confirmed the stoichiometry of Eq. 3.1 both in Solvesso 150 and in $CHCl_3$. The K'_{eq} values determined are shown in Table 3.6.

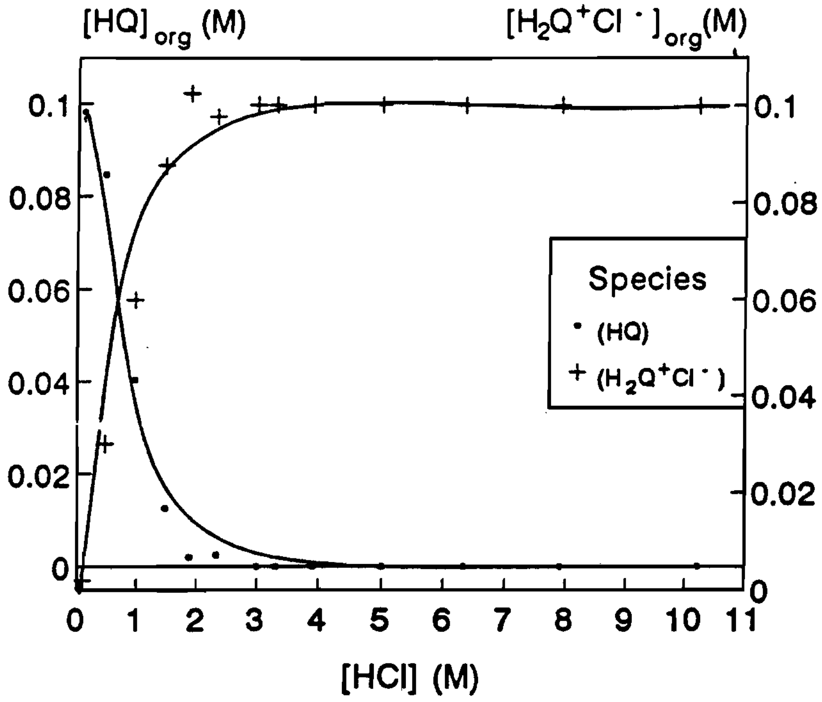

Figure 3.10 Speciation of the free, HQ, and protonated extractant, $H_2Q^+Cl^-$, as a function of HCl concentration in the aqueous phase (TN 1911 in $CHCl_3$).

The value of K'_{eq} indicates the relative basicity of the nitrogen atom present in those extractants. Therefore, the relative order of basicity in Solvesso 150 is as follows:

TN 2336 > TN 1911 > Kelex 100.

Fig. 3.12 shows the ability of TN 1911, TN 2336 and Kelex 100 to extract acid. As expected, under similar conditions, TN 2336, extracts more acid than TN 1911 and the difference between TN 1911 and Kelex 100 is small. Also, in Figs. 3.7 and 3.12, the reagents concentration have been calculated from the molarity found from perchloric acid titration in order to allow comparison of those reagents on a common basis. Using as a basis of comparison the molalities determined with copper loading, then, the degree of acid extracred by Lix 26 is considerably more than that extracted by TN 1911. The low purity of Lix 26 accounts for this and not some intrinsic property of the major active molecule itself.

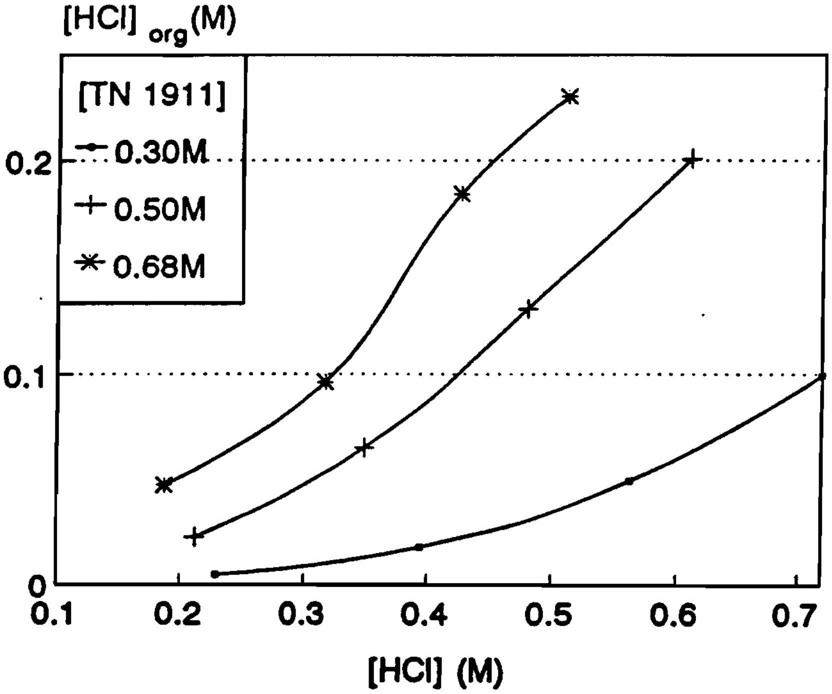

Figure 3.11 HCl extraction in low acid region $[TN\ 1911]_{org}$ = 0.30, 0.50 and 0.68M. Solvesso 150 and Tridecanol were present.

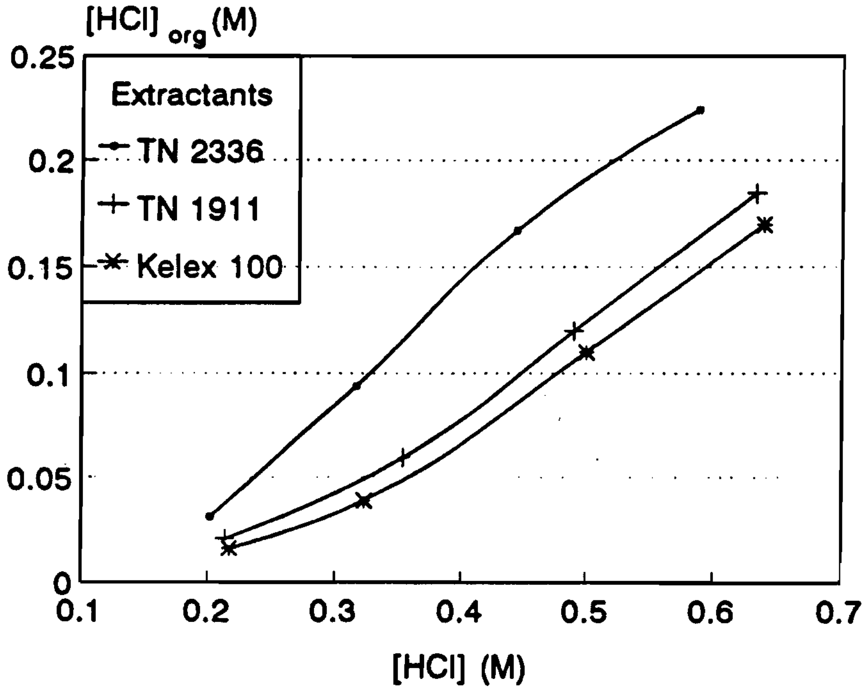

Figure 3.12 HCl extraction in low acid region $[\text{Extractant}]_{org}$= 0.50M and Solvesso 150 and Tridecanol were present.

Table 3.6 Log K'_{eq}[5] for HCl extraction at 25°C

	Solvesso 150		Chloroform	
	log K'_{eq}	K'_{eq}	log K'_{eq}	K'_{eq}
TN 1911	-0.33±0.01	0.49±0.02	-0.32±0.05	0.48±0.03
TN 2336	-0.26±0.01	0.55±0.02	N/A	
Kelex 100	-0.49±0.04	0.32±0.03	N/A	

N/A : not available.

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[5] The same correction was made here as per the footnot page 57.

3.4.8 Water Extraction in Low and High Acid Region

In Figure 3.13, the water concentration in the organic phase (0.50M TN 1911), $[water]_{org}$, has been plotted against the acid concentration in the organic phase. The [HCl] of the feeds used ranged from 0.2 to 8.0M. Solvesso 150 was used as diluent. This figure shows that the extent of water extraction depends on the solvent composition. Also, it was found that a pure solution of tridecanol was able to extract some water too. However, the amount of acid extracted was independent of the feed acidity but proportional to the modifier concentration. This graph also shows that for each mole of acid extracted in the organic phase, three moles of water are co-extracted when the TN 1911-Tridecanol-Solvesso 150 solvent is used. This suggests that acid is extracted in

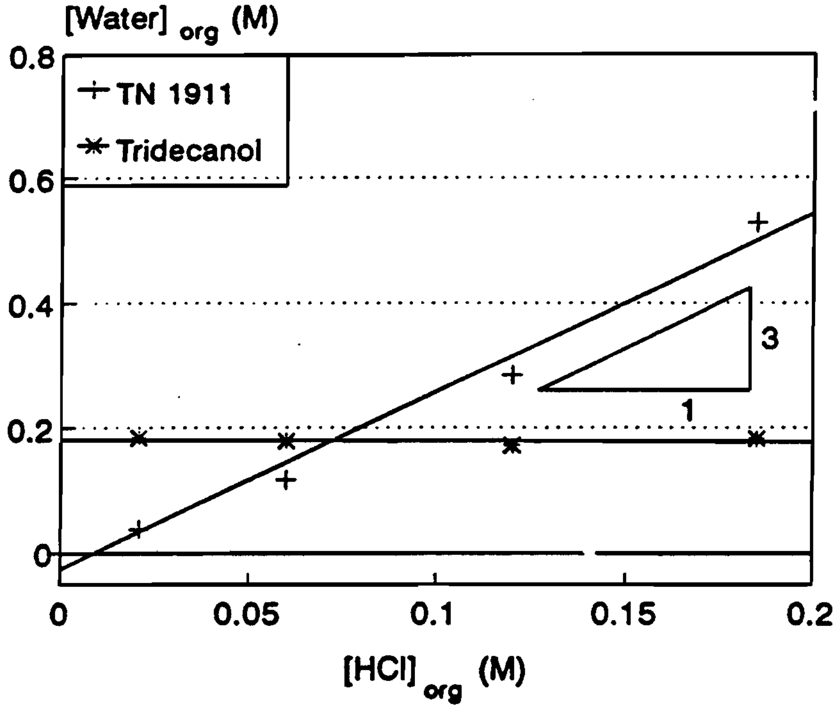

Figure 3.13 Water and acid extracted in low acid region. $[TN\ 1911]_{org}$ =0.50M, $[Tridecanol]_{org}$=1.58M and Solvesso 150 used as diluent.

hydrated form. Therefore, in Solvesso 150, the HCl extraction reaction can be written as:

$$HQ_{org} + HCl_{aq} + 3H_2O_{aq} \rightleftarrows [H_2Q^+Cl^- \cdot 3H_2O]_{org} \tag{3.2}$$

and the new extracted species would be $H_2L^+Cl^- \cdot 3H_2O_{org}$. Finally, similar results were found with TN 2336.

Figure 3.14 shows that water extraction is also diluent dependent. In chloroform, it was found that the water concentration in the organic phase was equal to $[HCl]_{org}$. Therefore, the HCl extraction reaction can be written as:

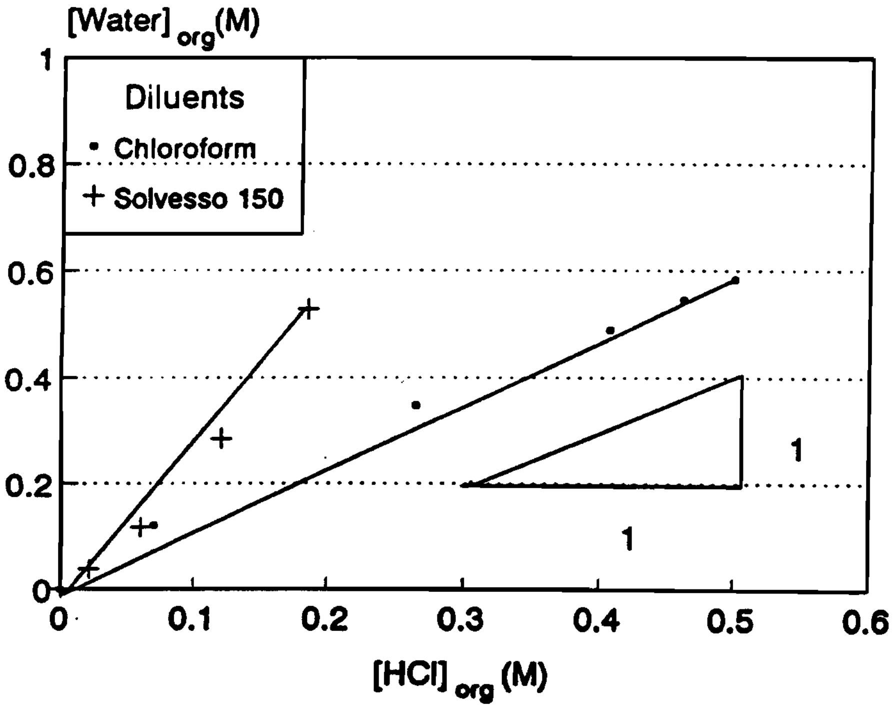

Figure 3.14 Water and acid extracted in low acid region. $CHCl_3$ and Solvesso 150 solutions of TN 1911 $[TN\ 1911]_{org}$=0.50M.

$$HQ_{org} + HCl_{aq} + H_2O_{aq} \rightleftarrows [H_2Q^+Cl^- \cdot H_2O]_{org} \quad (3.3)$$

Here, the difference in the dielectric constants of the two diluents accounts for the different amounts of water extracted. It is likely that chloroform solvated more efficiently the protonated extractant than Solvesso 150, whereas in Solvesso 150 solution tridecanol is solvating the protonated extractant more efficiently than the diluent. Besides, in chloroform solution, hydrogen bonds between water and the protonated species are less efficient since chloroform molecules are surrounding $H_2Q^+Cl^-_{org}$. On the other hand, in Solvesso 150 solutions, it is likely that formation of reverse micelles takes place in the organic phase. The latter involving the protonated extractant and the modifier leads to formation of water pools in the organic phase which explain the higher water content observed in this system. The modifier's role with respect to water extraction is depicted in Fig. 3.15. It was found, for pure tridecanol solutions in Solvesso 150, that the water content increases proportionally to the modifier concentration. However, the water content was independent of the feed acidity. When both the extractant and the modifier were present, then $[water]_{org}$ increases as $[HCl]_{org}$ increases. However, $[water]_{org}$ decreases slightly as the tridecanol concentration increases. As in Fig. 3.15, plots of $[water]_{org}$ vs. $[HCl]_{org}$ give a straight line of slope 3. These results clearly show that both the protonated extractant and the modifier are involved in the formation of the reverse micelles. Also, it is likely that the size and the abundance of those micelles depend on the concentration of those species. Besides, data suggest that the size of those micelles decreases as the modifier concentration increases most likely due to crowding effects caused by the high modifier concentration. Further investigations involving light scattering techniques will be needed to confirm this hypothesis.

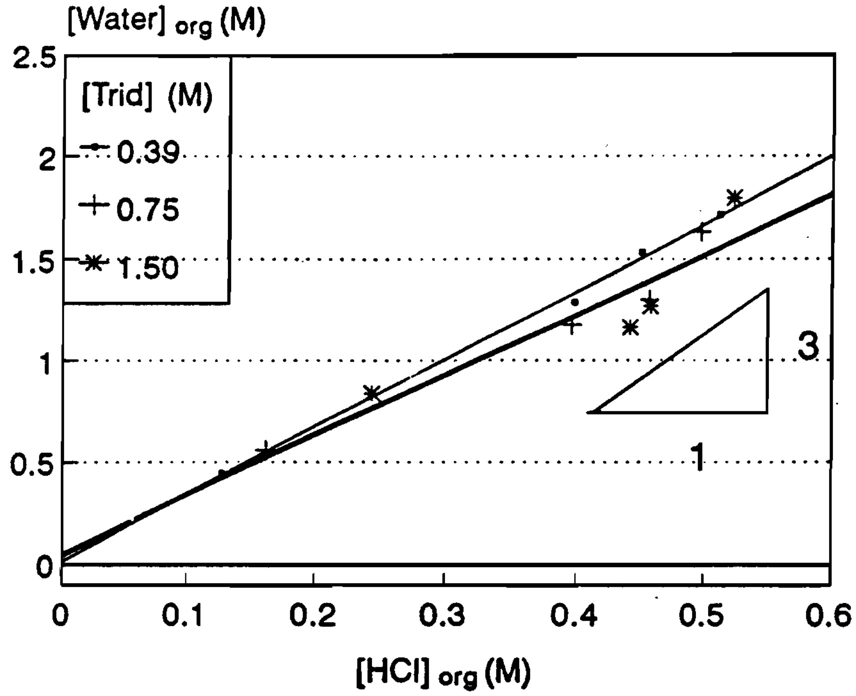

Figure 3.15 Water and acid extracted in high acid region. Solvesso 150 solutions of $[TN\ 1911]_{org}$=0.50M, $[Tridecanol]_{org}$=0.38, 0.75 and 1.50M.

3.5 Summary

Extensive characterization (IR, UV and ^{1}H-NMR spectroscopy) of non-commercially available TN 1911, TN 2181, TN 2221 and TN 2336 as well as commercially available 7-substituted-8-hydroxyquinoline was presented. The presence and nature of isomers found in purified extractants (TN 1911 and Lix 26) was confirmed by GC-MS and ^{1}H-NMR. Some structural analogies between Kelex (pre-1976) and TN 1911 were discussed. IR assignments of the main fundamental frequencies of the active substance in TN 1911 were discussed. The stoichiometry of the hydrochloric acid extraction reaction in $CHCl_3$ and Solvesso 150, the nature of the extracted species, as well as the acid extraction performances of various extractants were presented. The relationship between the water content in the organic phase and the amount of HCl extracted was established.

3.6 Acknowledgements

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Appendix A

Long-term Stability of the Extractant

In an industrial solvent extraction circuit the extractant is recycled continuously over a long period of time and any losses of it are replenished periodically. In view of the cost of these novel extractants it was decided to conduct some long term stability tests and measure the loss of the loading capacity of the extractants when these are in contact with concentrated HCl strip solution as is the latter which is consider to be the most aggressive environment for the organic extractants. The results obtained are summarized in Figure A.1.

The life expectancy was determined by loading the extractant with a copper solution at pH 4 in sulfate media (13) (see Chapter 3 section 3.4.6). This method has usually been used to determined the purity and the loading capacity of a given extractant. In Figure A.1 the percentage of copper extracted is the ratio of the initial amount of copper extracted by the reagent and the amount of copper extracted by the same reagent after being contacted with 8.12M HCl solution for a given time.

As it can be seen from that Figure, TN 2336 (the reagent possessing a saturated side chain) outperforms in stability TN 1911 (which has an unsaturated side chain). It is thought that the degradation of the reagent is due in part to the breakage of the double bond present in the side chain which in turns lead to the solubilization of the reagent into the aqueous phase. Finally, it must be explained

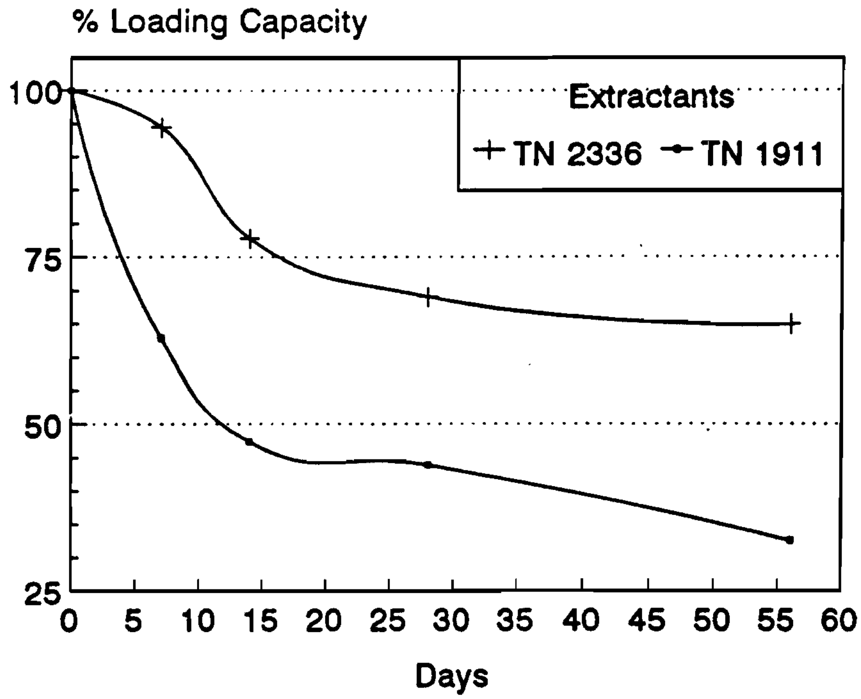

Figure A.1 Long term chemical stability of 8-HQ extractants against HCl attack.

that the time (in days) given in Figure A.1 does not means represents the real life expectancy of the extractant. This is so because in a SX circuit the stripping stage represents no more than one third of the full cycle of the extractant within the SX circuit. In other words, the useful life of the extractant would probably be a least a factor of 3 larger.

Chapter 4

Pd(II) Extraction Equilibria and Stripping[1]

4.1 Abstract

Equilibrium measurements of palladium extraction by chloroform solutions of 7-substituted-8-hydroxyquinoline derivatives from aqueous chloride media demonstrated that palladium is extracted as the chelate PdQ_2. The formation of the chelate PdQ_2 was also confirmed with direct spectroscopic analysis. The extraction equilibrium constants, K_{ex}, were determined to be log K_{ex}=5.59 and 5.84 for TN 1911 (an unsaturated and sterically-hindered derivative) and TN 2336 (a saturated and sterically-free derivative) respectively. It was found that PdQ_2 exhibits an absorption band at 460 nm in chloroform. It was shown that palladium extraction is influenced by both the extractant concentration and reagent structure. The importance of steric over electronic effects with respect to metal extraction was discussed. The individual roles of palladium, proton and chloride ion concentration were demonstrated. It was found that palladium extraction is exothermic with an enthalpy change of -29.6 kJ/mol. The influence of stripping agent composition with respect to metal stripping was investigated. The addition of $MgCl_2$ in the HCl strip solution was found to enhance stripping performance.

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[1] This chapter has been accepted as an article for publication in Solvent Extraction and Ion Exchange, 12(2), (1994). Reprinted from Ref. 12(2) by courtesy of Marcel Dekker inc.

4.2 Introduction

In part 1 of this series of publications [Chapter 3], Côté and Demopoulos (1) have reported the characterization of a number of newly synthesised 7-mono-substituted alkyl or alkenyl derivatives of 8-hydroxyquinoline (8-HQ). These extractants, proprietary products of Schering Berlin, A.G. (Germany) are labelled: TN 1911, TN 2181, TN 2221 and TN 2336. The reason for synthesizing these reagents was to design extractants specific for platinum group metal separation.

At McGill University, research has been undertaken over the last few years to develop new solvent extraction methods for the separation of PGM using alkylated derivatives of 8-HQ as the preferred family of extractants. This research has led to a patented (2) method of separating Pt(IV) from Pd(II) via co-extraction and differential stripping. Among the commercial reagents tested and advocated for use were Kelex 100 (3), Lix 26 (4) and more recently, TN 1911 (5).

The objective of this communication is to present the fundamental chemistry of Pd(II) extraction with 8-hydroxyquinoline derivatives in the 8-HQ-HCl-$MgCl_2$ system.

4.3 Experimental

In this investigation, four 8-hydroxyquinoline extractants were used, namely TN 1911, TN 2181, TN 2221 and TN 2336. All 8-HQ reagents were supplied by Schering Berlin AG., Bergkamen, Germany.

Purification of the "as received" extractant consisted of contacting a 0.30M solution of the extractant with an equal volume of 1.42M HCl for 3 consecutive times. This was followed by several washings with equal volumes of water until no chloride was detected in the wash water.

In most of the cases, the extractants were diluted with Solvesso 150 (a Exxon Chemicals Ltd. proprietary diluent with 97% aromatic content) and extraction, with TN 1911 and TN 2336 was investigated in the tridecanol-Solvesso 150 system. Here, to study the [Cl^-] effect, the HCl concentration was kept constant at 1.00M and the total chloride ion concentration was varied by $MgCl_2$ addition. This salt was used because it does not form extractable anionic chloro-complexes since magnesium does not have *d* electrons to form such complexes. In addition, it cannot be extracted as Mg^{2+}. Finally, large quantities of this salt do not interfere with palladium analysis by atomic absorption.

The effect of [H^+] was studied under the following conditions: the total chloride ion concentration was kept constant at 1.00M (as HCl) and the proton concentration was varied by addition of H_2SO_4. Sulfuric acid was chosen because sulfate does not form extractable anionic complexes with Pd^{2+}. However, HNO_3 cannot be used since it may oxidize the extractant. Finally, sulfuric acid was considered as a mono acid to calculate the free concentration of proton in solution. Therefore, the H^+_{free} concentration is the sum of protons coming from hydrochloric acid and those from the first dissociation of sulfuric acid.

The metal concentrations in the feeds and raffinates were determined by atomic absorption, after spiking the sample with $LaCl_3$. An air-acetylene flame was used for palladium determination. Hydrochloric acid titrations in aqueous solutions were performed with an automatic titrator at a pre-selected end-point set at pH 7.00. Analytical grade 0.100M NaOH was used as titrant.

4.4 Results and Discussion

In this work, two types of experiments were conducted: those involving chloroform solutions of the 8-HQ derivatives and those which involved solutions of 8-HQ in tridecanol-Solvesso 150. The former part of the work focused on measuring the fundamental properties of the Pd(II)-8-HQ system, while the latter focused on measuring the extraction/stripping performance of the 8-HQ derivatives using the industrial solvent system, tridecanol-Solvesso 150.

4.4.1 Reagent Characterization

Figure 4.1 shows the general structure of 8-HQ derivatives and Table 4.1 outlines some key features of the 8-HQ derivatives. Kelex 100 is included in this list as a reference material.

Table 4.1 Some features of the 8-HQ derivatives

	R Group				Steric Hindrance	
Reagent	Sat (1)	Unsat (1)	# Carbon	Isomer	Low	High
TN 1911		X	10-13	Y		X
TN 2181		X	10-13	?	X	
TN 2221	X		10-13	?		X
TN 2336	X		10-13	?	X	
Kelex 100	X		11	N	X (2)	

(1) The abbreviations "sat" and "unsat" refer to saturated and unsaturated R group respectively; (2) medium steric hindrance.

It is the nature and the orientation (conformation) of the side chain, R, that characterizes the various extractants. For example, in the case of TN 1911 the side chain is oriented towards the two bonding sites, namely the phenol and the nitrogen heteroatom, which causes a high steric hindrance. However, the R group in TN 2336 is oriented away from the bonding sites, thus giving an extractant with low steric hindrance. At the same time, the presence or absence of double bonds in the substituent group alters the reactivity of the reagent, thus altering the extraction properties.

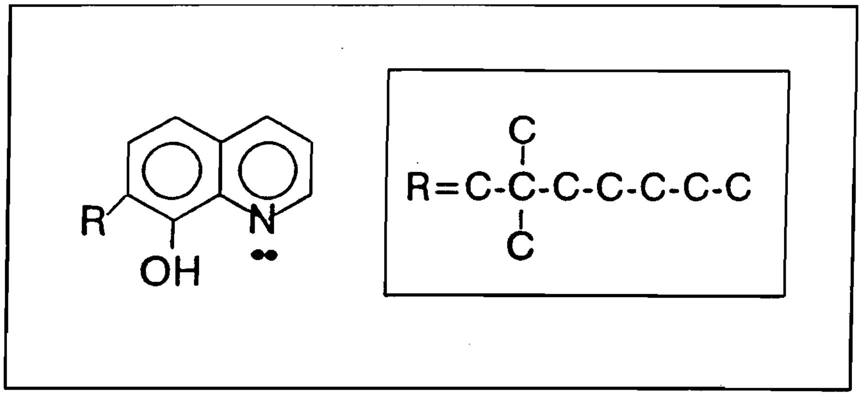

Figure 4.1 The general structure of 7-substituted 8-Hydroxyquinoline derivatives.

A complete characterization of the above-mentioned reagents is reported in part 1 (1) [Chapter 3].

4.4.2 The Pd(II)-HCl-$MgCl_2$-8-HQ-Chloroform System

4.4.2.1 The Stoichiometry of the Extraction of Pd(II) with 8-HQ Derivatives

The equilibrium distribution coefficient of Pd(II), D_{Pd}, was measured in chloroform solutions of 8-HQ over the following conditions: [Pd(II)] ranging from 5×10^{-5} to 2×10^{-4} M, [TN 1911] and [TN 2336] ranging from 2×10^{-3} to 2×10^{-2} M, $[H^+]$ ranging from 0.3 to 2.0 M and $[Cl^-]$ ranging from 0.5 to 2.0M.

Figures 4.2 to 4.4 show the effect of [HQ], $[H^+]$ and $[Cl^-]$ respectively on D_{Pd}. The plotted data points lie on straight lines of slope 2.05 ± 0.04, -2.09 ± 0.09 and -3.9 ± 0.1 for TN 1911 and 1.9 ± 0.1, -2.1 ± 0.1 and -4.0 ± 0.1 for TN 2336 respectively. The respective data with reference to [Pd(II)] gave a slope 0 (not shown). This was expected since very large excess of extractant was used to

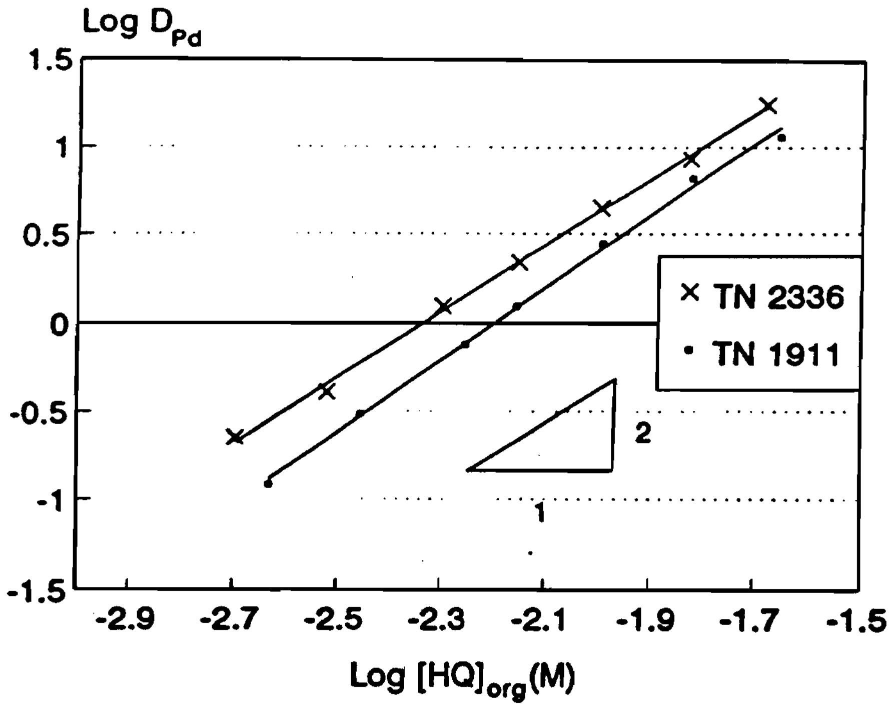

Figure 4.2 Log D_{Pd} as a function of log [Extractant] in $CHCl_3$.

perform the slope analysis study. Figures 4.3 and 4.4 show that Pd(II) extraction is suppressed at high $[H^+]$ or $[Cl^-]$. Similar observations were reported by other authors for Kelex 100 (6) and 2-methyl-8-HQ (7). From the dependence of D_{Pd} on the above mentioned parameters, the extraction reaction of the present system is deduced to be:

$$PdCl_4^{2-} + 2HQ_{org} \rightleftarrows PdQ_{2org} + 2H^+ + 4Cl^- \tag{4.1}$$

Consequently, D_{Pd} is expressed as:

$$D_{Pd} = K_{ex}[HQ]^2_{org} / [H^+]^2[Cl^-]^4 \tag{4.2}$$

The subscript "org" denotes species in the organic phase. The equilibrium constant, K_{ex},, for the two extractants was calculated from the following equation:

$$\log K_{ex} = \log D_{Pd} - 2\log [HQ]_{org} + 2\log[H^+] + 4\log[Cl^-] \tag{4.3}$$

assuming that $PdCl_4^{2-}$ was the predominant Pd(II) species present in the aqueous phase. The log K_{ex} values calculated for TN 1911 and TN 2336 are given in Table 4.2 along with the corresponding values for Kelex 100 and 2-methyl-8-hydroxyquinoline. It seems that within experimental error TN 2336 and Kelex 100 have the same affinity for Pd(II). However, 2-methyl-8-HQ differs from the rest having a stronger affinity for Pd(II) since its substituent is not only small (a methyl) but is also in 2-position, thus lowering the steric hindrance with respect to the phenol group.

Table 4.2 Extraction equilibrium constants of Pd(II) with some 8-HQ derivatives

Extractant	log K_{ex}	Ref
TN 1911	5.59±0.05	This work
TN 2336	5.84±0.05	This work
Kelex 100	5.86±0.06	6
2-methyl-8-Hydroxyquinoline	6.39	7

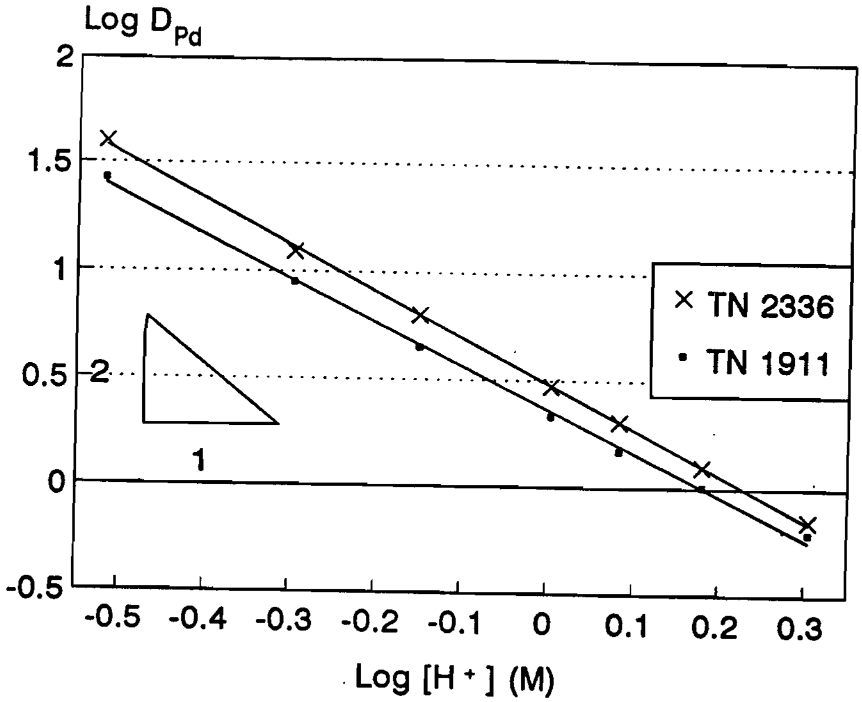

Figure 4.3 Log D_{Pd} as a function of log $[H^+]$ in $CHCl_3$.

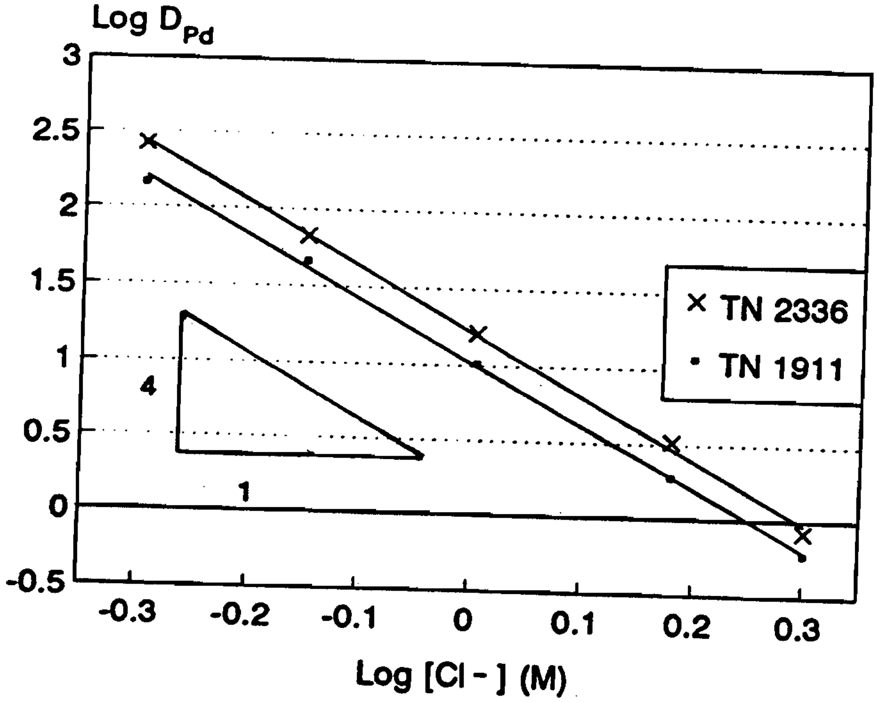

Figure 4.4 Log D_{Pd} as a function of log $[Cl^-]$ in $CHCl_3$.

4.4.2.2 Spectroscopic Characterization

UV-Visible Characterization

UV spectra of $PdCl_4^{2-}$ in HCl solution, tridecanol in chloroform, and Pd(II) loaded TN 1911 and TN 2336 (PdQ_2) in chloroform were recorded [see Appendix B at the end of this chapter]. The UV spectra of the unloaded 8-HQ derivatives have already been published elsewhere (1) [Chapter 3]. In general the maximum absorption wavelength of all unloaded 8-HQ derivatives, diluted in chloroform, was located at about 248.0 nm (1).

The spectrum of $PdCl_4^{2-}$ was found to exhibit two absorption bands located at 222.7 and 279.7 nm respectively. These absorbance values are in good agreement with those reported by Elding (8) who has extensively studied palladium chloro-complexes in HCl media.

Tridecanol displays an absorption band at 243.9 nm. Chloroform solutions of TN 1911 and TN 2336 were successively contacted with several portions of fresh Pd(II) solutions to obtain a fully loaded organic solvent. UV study of the organic phases after each loading with Pd(II) displayed two absorption bands located at 265.4 nm, and 460.0 nm respectively. The intensity of the 460.0 nm absorption band increased as the number of loadings was increased. This absorption band is obviously associated with the chelate, PdQ_2, formed between TN 1911 and TN 2336 with Pd(II). Similar observation has also been reported by Al-Bazi and Freiser for the chelate complex formed between Kelex 100 and Pd(II) (9). The 265.4 nm band, the absorptivity of which ($\log \epsilon = 5.41$) was much larger than that of the 460.0 nm ($\log \epsilon = 3.74$), is thought to be due to an impurity present in the organic phase. Table 4.3 summarizes the maximum wavelengths and the absorptivity, ϵ, of each of the above mentioned species in chloroform solution.

Table 4.3 UV-Visible maximum wavelengths of $PdCl_4^{2-}$(aq), tridecanol and PdQ_2 chelates in chloroform

Species	log ϵ	λ_{max} (nm)	Ref
$PdCl_4^{2-}$	4.448	222.0	This work
tridecanol	0.398	243.9	This work
8-HQ (TN 1911)	4.68	248.8	This work
PdQ_2 TN 1911	3.74	460.0	This work
unknown	5.41	265.4	This work
PdQ_2 TN 2336	3.81	460.0	This work
unknown	5.41	265.4	This work
PdQ_2 Kelex 100	N/A.*	460.0	9

* Not available.

Infrared Characterization

The infrared spectrum of neat TN 1911 has already been published in Part 1 (1) [Chapter 3]. It is a fairly complex spectrum. Nevertheless, most of the bands have been assigned. The aim of the authors in the present study, was to find the frequencies associated with the Pd-O and Pd-N bonds respectively. However this proved impossible within the 400-4000 cm^{-1} studied. Taking as a basis the relationship established by Ohkaku and Nakamoto (10) between the M-O and M-N stretching frequencies and the atomic number of the metal for MQ_2 type complexes the respective frequencies for Pd-O and Pd-N bonds are estimated to be below 200 cm^{-1}. This seems to explain then why the Pd-O and Pd-N bonds were not observed in the frequency range studied.

On the other hand, examination of a chloroform solution of TN 1911 contacted several times with fresh portions of $PdCl_4^{2-}$ solution showed that the intensity of the O-H band located at about 3390 cm^{-1} markedly decreased as the amount of Pd(II) present in the organic phase increased. This should be seen as an indirect proof that the oxygen atom of the oxine is involved in the formation of the chelate PdQ_2.

4.4.3 The Structure of Chelates of the Type MQ_2

It has been known (11-13) that the chelate formed between Cu^{2+} and 8-hydroxyquinoline exists as dimorphic, α and β, species in both the anhydrous, CuQ_2 and dihydrate, $CuQ_2.2H_2O$ forms. Kruh and Diwiggins (11) have reported that copper coordinates with two oxygen and two nitrogen atoms of the 8-hydroxyquinoline to form a square-planar chelate. They also found that two water molecules were weakly bound above and below the copper. Suito and Sekido (12) described the α and β forms of $CuQ_2.2H_2O$. The first one, of fibrous morphology, was metasable and converted into the stable β form. X-ray powder diffraction study of the two forms showed a probable difference in the structure.

Merrit et al. (13) have studied the β form of $CuQ_2.2H_20$ and have concluded that it was similar to $ZnQ_2.2H_2O$. According to Hoy and Morriss (14), Jonassen has found that two anhydrous forms of ZnQ_2 exist; the α form was unstable and transformed into the stable β one. Charles et al. (15) have shown that infrared spectroscopy allowed for the identification of both forms. The complete structure of CuQ_2 in its β form was elucidated by Palenik (16) and finally, Hoy and Morris (14) have established the α form. Now, it is well established that both forms of MQ_2 and $MQ_2.2H_2O$ are *trans* planar molecules.

4.4.4 PdQ_2 Chelate Structure

It is likely that the palladium chelate formed with 8-hydroxyquinoline and its 7-substituted derivatives has structure similar to that of the copper chelate. In $PdCl_4^{2-}$, Pd^{2+} has a $4d^8$ electronic configuration and forms a square planar chloro-complex as does $CuCl_4^{2-}$. The chelate complex formed between $PdCl_4^{2-}$ and 8-HQ should be planar and the Pd^{2+} ion should lie in the centre of two co-planar five-member rings. Additionally, the two oxine rings should lie almost in the same plane. However, the presence of bulky substituents in the 7-position are expected to distort the oxinate.

The planarity and the bond angles in the chelate mean that the oxygen atom must be sp^2 hybridized and therefore has a lone pair of electrons in the plane of the molecule at about 120° to the C-O bond. Similar spatial arrangement has been found in the simple phenol molecule. The nitrogen atom is also sp^2 hybridized. This is essential to maintain the oxine ring planar. This provides formation of sigma, σ, bonds between the donor atoms and the metal centre. The bonds formed are essentially covalent. However, the bond between the nitrogen and the Pd^{2+} is a dative one (→) because the electron doublet is provided only by the nitrogen. The Pd-O bond is expected to be shorter and stronger than that between $Pd \leftarrow N$. Similar observations, based on X-ray studies, have been reported for the copper chelate. A mass spectrometry study of several chelates formed between divalent metals, including Pd(II), and 8-hydroxyquinoline, however, has been reported by Kidani et al. (17) suggesting otherwise. From the fragmentation sequences reported, it was suggested that the bond formed between the metal centre and the nitrogen atom was stronger than that formed between the oxygen and Pd^{2+}.

4.4.5 The Relationship between Extractant Structure and Pd(II) Extraction

The chelating power of 8-HQ derivatives can be modified either by changing the inductive effect on the nitrogen and hydroxyl group via the introduction of substituents in the oxine skeleton, or by causing steric effects near the functional group, i.e. in the 2- and 7-position in the oxine ring system. Irving and Rossotti (18) have reported that pK_{OH} was increased by alkyl substitution in the 2-, 5- and 7-position of the oxine system. Here, pK_{OH} and pK_{NH} are defined as the negative logarithm of the respective dissociation constants. This is in accord with the expected inductive effect since the methyl group would release electrons towards the most electronegative atom, the oxygen, thus reducing the ionic character of the O-H bond of the phenol group. Irving and Rossotti (18) also reported that the value of pK_{NH} was increased by alkyl substitution, in the 2- or 5-position in the oxine. The lowering of pK_{NH} in the 7-position was explained by the displacement of the hydroxyl group by the methyl substituent towards the basic nitrogen atom, thus hindering the approach of proton.

The same authors (18) also attempted to correlate the stability constants of several chelate complexes, MQ_2, with the proton dissociation constant of the phenolic function, pK_{OH}. The last statement of Irving and Rossotti (18) implied that the authors, at that time, did not realize the importance of intramolecular hydrogen bonding present in such molecules. In fact, this will be the cornerstone of the coming discussion. Similar reasoning has been used by Dalton and Price (19) to explain the extraction power of some *o*-hydroxyoximes.

Electronic effects are of two kinds. The inductive effect associated either with electron-releasing or electron-withdrawing substituents and the resonance effect which is the property of π electrons to be delocalized through either an aromatic ring system and/or through conjugated double bonds. In the latter case, at least one unsaturation must be present in the side chain. The steric effect is associated with the position of the substituent group on the oxine ring, its spatial orientation and its size.

Let us examine in detail the structure of the extractant and the influence of electronic and steric effects on Pd(II) extraction. Figure 4.5 shows the ability of the various reagents to extract Pd(II) from hydrochloric acid solution ([HCl] = 1.42M).

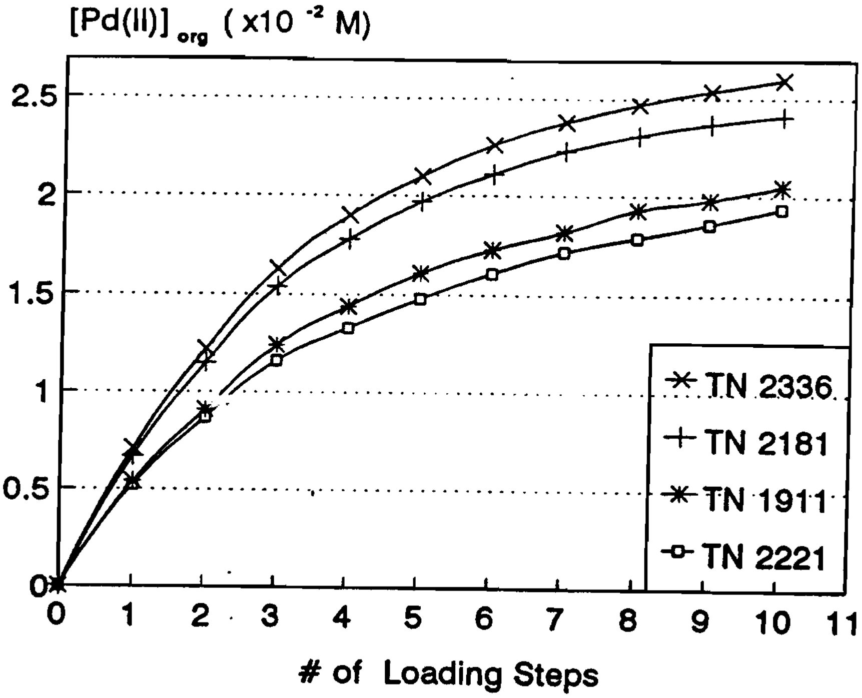

Figure 4.5 Extraction of palladium as a function of the number of consecutive loading steps CT 30 min.

Here, saturation of the extractants was sought in a cross-current loading mode. It is seen that TN 2336 is the most effective extractant. Also, when the data for TN 2336 are compared with those of TN 2221 it is evident that steric hindrance plays a more important role, with respect to Pd(II) extraction, than electronic effects. In the case of TN 2336 and TN 2221, both extractants have a saturated substituent group. Therefore, they do not experience inductive electronic effect due to an unsaturation. Nevertheless, they experience some resonance, but this plays a marginal role in Pd(II) extraction. This is depicted in Figure 4.5 when comparing data of TN 2336 with TN 2181 and those of TN 1911 with TN 2221.

4.4.5.1 Steric Effects

According to Table 4.1, TN 2336 and TN 2221 (both carrying a saturated R group) experience low and high steric hindrance respectively. The latter is caused by the substituent group in the 7-position which pushes the phenolic proton towards the nitrogen atom thus increasing intramolecular hydrogen bonding between the proton and the nitrogen atom. Rossotti and Rossotti (20) have reported that such strong hydrogen bonding is also present in the unsubstituted 8-HQ. Similar observations were reported by Ashbrook (21) for Kelex 100, an other well known 7-substituted 8-HQ derivative.

The intensity of intramolecular hydrogen bonding can be measured by infrared spectroscopy. As it can be seen from Table 4.4, the fundamental stretching frequency, ν, of the hydroxyl function decreases as the steric hindrance, caused by substitution in the 7-position, increases. This is a strong indication of increasing strength of intramolecular hydrogen bonding in substituted 8-hydroxyquinoline derivatives with respect to the parent unsubstituted 8-hydroxyquinoline. On the basis of the intramolecular hydrogen bonding phenomenon, the extraction power of the tested derivatives can be interpreted. By comparing the data of Figure 4.5 with the spectroscopic data in Table 4.4, it is seen that there is a relationship between the extraction power of the extractant and the strength of the intramolecular hydrogen bonding. Thus, the strongest extractant, TN 2336, experiences the weakest intramolecular hydrogen bonding and hence the lowest steric hindrance. On the other hand, the weaker extractant, TN 2221, is experiencing the strongest steric interaction as shown by strong intramolecular hydrogen bonding. This is an example of the Thorpe-Ingold effect (22) according to which strong hydrogen bonding provides a means of stabilizing the close proximity of those atoms brought about by steric hindrance.

Finally, the position of the double bond will influence the steric effect as well. The steric hindrance can be considerable if the oxine ring and the rest of the side chain are in *cis* position with respect to the bond. In the *trans* isomer however the steric hindrance is less intense. TN 1911 is known to be a mixture of isomers as was discussed in part 1 (1) [Chapter 3]. However, the exact nature of the isomers present, i.e. *cis* and *trans* was not determined nor were the other reagents like TN 2336 analyzed for isomers and thus only a limited discussion can be offered in this regard.

4.4.5.2 Electronic Effects

Despite the fact that electronic interactions are relatively weak with respect to metal extraction, it is worth explaining these effects and rationalizing them with respect to palladium extraction. From the inductive effect point of view, all 8-HQ derivatives are similar. Here, the increase of electronic density due to a double bond present in the side chain is almost negligible when compared to that caused by a saturated one. Besides, the size of the substituents is similar.

From the resonance effect point of view however, unsaturated derivatives

Table 4.4 Fundamental stretching frequencies of O-H bond in the 8-HQ reagents

Extractant	ν (cm^{-1})	Solvent	Ref.
8-hydroxyquinoline	3419	CCl_4	20
2-methyl-8-hydroxyquinoline	3415	CCl_4	20
7-substituted-8-hydroxyquinoline			
Kelex 100	3410	CCl_4	21
Kelex 100	3395	Neat	1
TN 2336	3395	Neat	1
TN 2181	3400	Neat	1
TN 1911	3370	Neat	1
TN 2221	3370	Neat	1

will be more stabilized than the saturated ones. However, this is possible only when the double bond is in α-position with respect to the ring. At this position, the unsaturation becomes conjugated with the ring and therefore increases the number of hybrids thus contributing to further stabilization of the extractant.

In this regard then the slightly better extraction performance of TN 1911 (unsaturated derivative) *vis-à-vis* TN 2221 (saturated) is understood, since the former has an unsaturation in α-position with respect to the ring system (1). However, this is not the case with the homologous pair of TN 2181 (unsaturated) and TN 2336 (saturated) since TN 2181 exhibited slightly inferior extraction power than TN 2336.

In general, at the phenolic bonding site, it is known that the phenol group lies in the plane of the ring. Therefore, the oxygen atom is sp^2 hybridized and one lone pair of electrons is delocalised on the oxine ring system. The inductive effect due to an electron releasing substituent increases the electronic density on the oxygen thus reducing the ionisation of the proton which produces the corresponding phenoxide ion. But, the phenoxide anion is more stable than the unionised phenol since it is further stabilized by resonance. Here, the oxygen shares more than one lone pair with the ring thus providing more resonance hybrids which further contribute to stabilize the phenoxide moieties. The net effect of resonance is therefore to stabilise the phenoxide moiety to a greater extent than the phenol and thus to favour also the ionisation of the proton.

From the metal extraction point of view, an electron-releasing substituent will decrease the extraction power of the extractant due to its inductive effect on the O-H bond. However, resonance will operate in the opposite way because it decreases the electronic density on donor atom. Overall, the presence of an electron-releasing substituent will exercise a net positive or negative effect on the extraction power of the extractant depending on which of the two electronic effects (inductive or resonance) dominate and whether it is the Pd-O or the Pd←N bond which is stronger.

At the nitrogen atom site, the induction caused by an electron-releasing substituent increases the basicity of the nitrogen atom thus increasing the reagent extraction performance. However, like pyridine, the lone pair of electrons of the nitrogen heteroatom experiences resonance which in turns decreases the electronic density of this atom and hence decreases the extraction power of the extractant. Again, in this case the net effect will be determined by the dominant electronic effect, i.e. inductive (positive here) versus resonance (negative).

In summary, an electron releasing substituent will exercise a negative inductive/positive resonance effect on Pd-O bond and a positive inductive /negative resonance effect on the Pd←N. The overall electronic effect could be either positive or negative on the extraction power of the extractant depending on the relative strength of the two bonds, i.e. Pd-O and Pd←N. Nevertheless, the electronic effects seem to be overall inferior to the steric hindrance caused by the substituent groups.

4.4.6 The Pd(II)-HCl-8-HQ-Tridecanol-Solvesso 150 System

All of the data reported so far, with the exception of Figure 4.5, were collected using chloroform solutions of each of the 7-substituted 8-HQ investigated. However, industrial solvent extraction does not make use of chloroform and a different formulation must be used. In the case of PGM extraction with commercial 8-HQ extractants, it has been already established (4) that the extractant should be diluted in an aromatic diluent, namely Solvesso 150, along with a long chain alcohol, such as isodecanol or tridecanol used as phase modifier. Thus in the rest of this paper, the parameters which influence the extraction of Pd(II) from chloride solutions with 8-HQ derivatives are studied in the system Extractant-Tridecanol-Solvesso 150.

4.4.6.1 Parameters that Influence Pd(II) Extraction.

The Organic Phase Composition

The extractant concentration in the organic phase influences the extent of metal extraction. Figure 4.6 shows the relationship between D_{Pd} as a function of TN 1911 concentration and time. From this figure, it is seen that in general equilibrium was reached within 30 minutes.

Finally, pure solutions of tridecanol diluted either in chloroform or Solvesso 150 were extensively contacted with Pd(II) solutions of various acidities (from 0.1 to 10 M) and it was found that this phase modifier is unable to extract Pd(II).

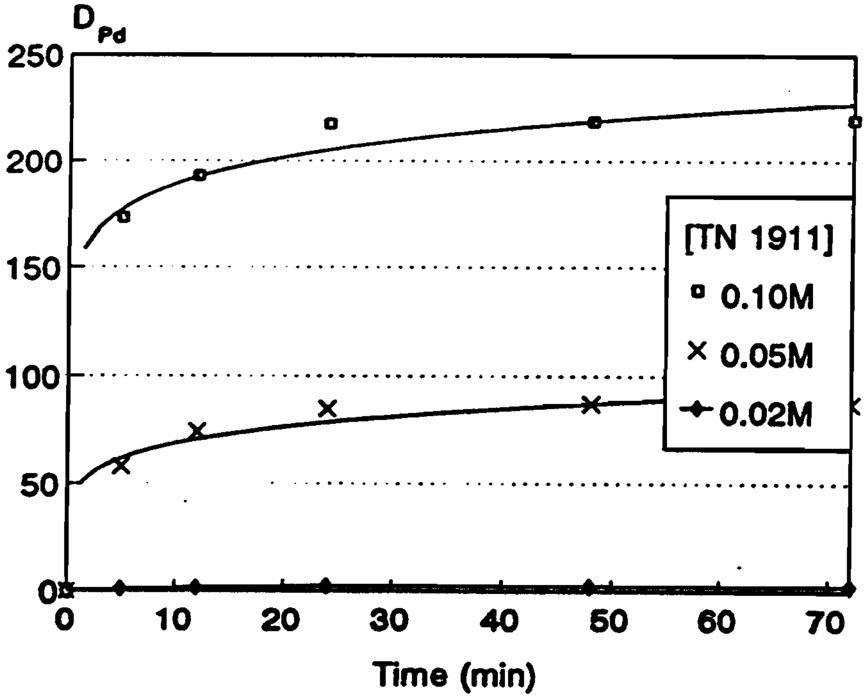

Figure 4.6 Palladium distribution coefficient as a function of $[\text{TN 1911}]_{org}$ and time.

The Feed Composition

Figure 4.7 shows that as the feed acidity is increased, the extraction of Pd(II) decreases accordingly for both extractants. Besides, this continuous decrease suggests that the chelate complex, PdQ_2, is the only one formed in the organic phase. A similar observation has been made for Pd(II) extraction with Kelex 100 (6).

The individual effect of proton and chloride ion concentration on Pd(II) extraction, with TN 1911 and TN 2336, is depicted in Figure 4.8. The effect of chloride ion is stronger than that of the proton on Pd(II) extraction. The strong decrease of palladium extraction due to chloride addition can be explained on the basis of two effects. Firstly, the activity of proton is increased by $MgCl_2$ addition (23). Secondly, Le Chatelier's principle readily accounts for the fact that palladium extraction is suppressed by the increased concentration of products, namely H^+ and Cl^- (Eq. 4.1). As Eq. 4.2 states, the distribution coefficient of Pd(II) is more strongly inversely proportional to $[Cl^-]^4$ (power 4) than $[H^+]^2$ (power 2). Finally it should be added that the activity of protons is much lower in H_2SO_4 (24) than in HCl media (23) of the same normality and this further contributes to the weakening of the H^+ effect on Pd(II) extraction.

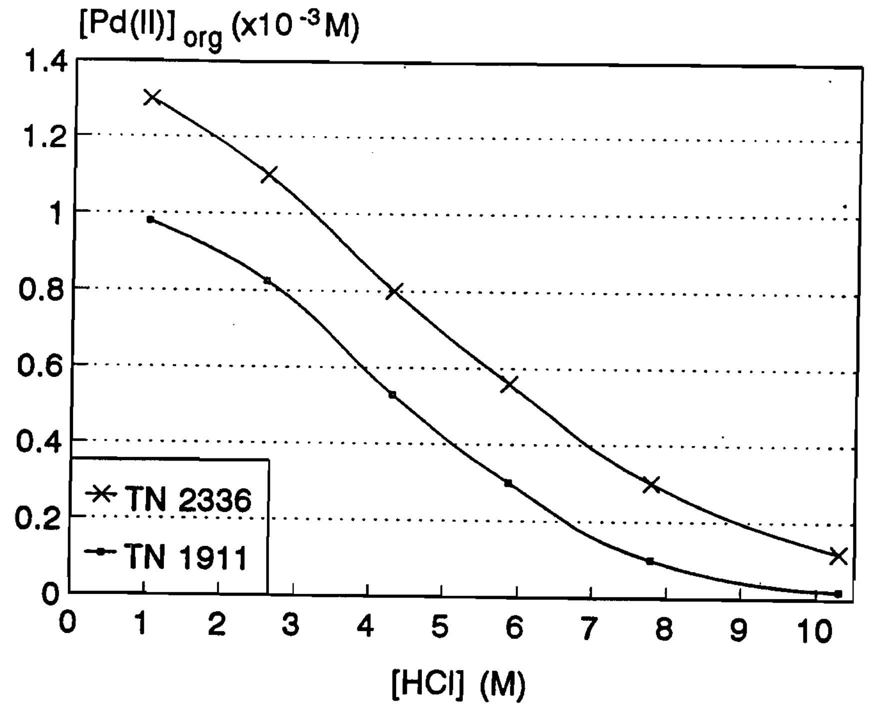

Figure 4.7 Extraction of palladium as a function of HCl concentration.

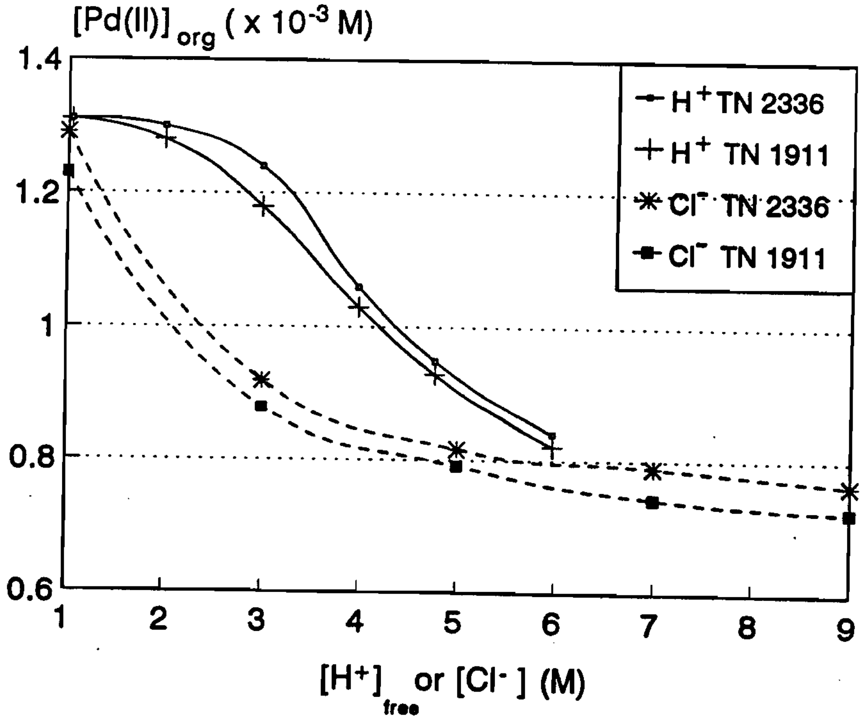

Figure 4.8 Extraction of palladium as a function of H$^+$ and Cl$^-$ concentration.

The Effect of Temperature on Pd(II) Extraction

Tests were performed to evaluate the effect of temperature on Pd(II) extraction with TN 1911. The distribution of palladium as a function of temperature and time is presented in Figure 4.9. The data are displayed in a semi-logarithmic scale. From this figure, it can be seen that D_{Pd} decreases as the temperature increases.

Further treatment of the equilibrium data of Figure 4.9 at equilibrium (90 min contact time) allowed us to evaluate the enthalpy change, $\Delta H°$, for Pd(II) extraction, assuming that Pd(II) is extracted according to reaction 4.1. Thus since [HQ], $[H^+]$ and $[Cl^-]$ were kept constant when the temperature effect was investigated we can use log D_{Pd} in the place of log K_{ex} (see Eq. 4.3) and analyze the data with the integrated Van't Hoff equation:

$$\log D_{Pd} = -\Delta H°/2.3RT + \text{constant} \tag{4.4}$$

The Van't Hoff plot is shown in Figure 4.10. An enthalpy change of -29.6 kJ/mol was determined indicating that the extraction of palladium is exothermic. The enthalpy change found for the Pd(II)-TN 1991-tridecanol-Solvesso 150 system is negative. An enthalpy change of the same sign has been found by Kelebek and Demopoulos (25) for the Au(III)-Kelex 100-tridecanol-Solvesso 150 (-58.6 kJ/mol). This suggests that extraction should be carried out at ambient temperature and stripping at elevated temperatures.

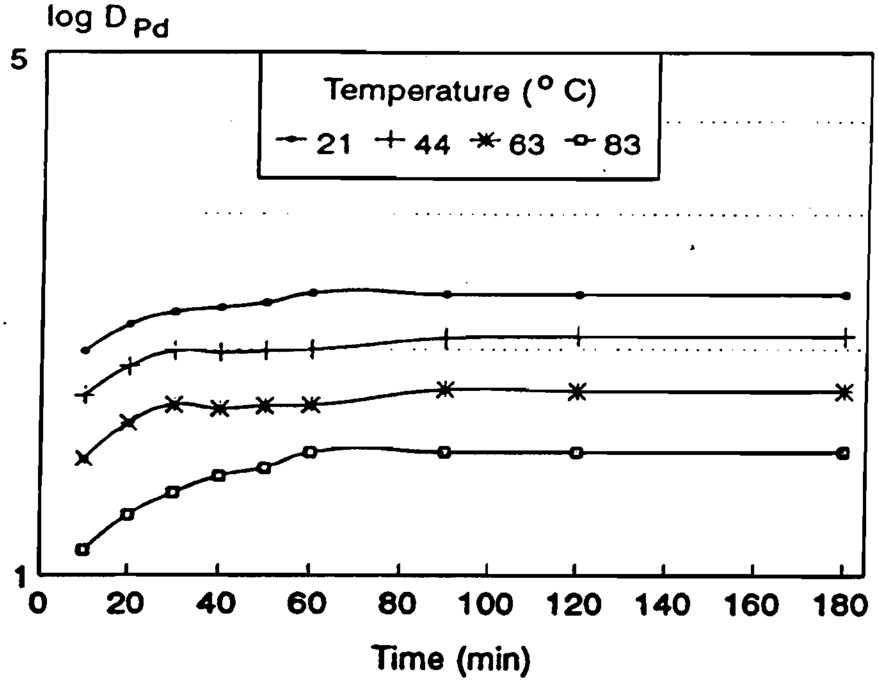

Figure 4.9 Palladium distribution coefficient as a function of temperature and time.

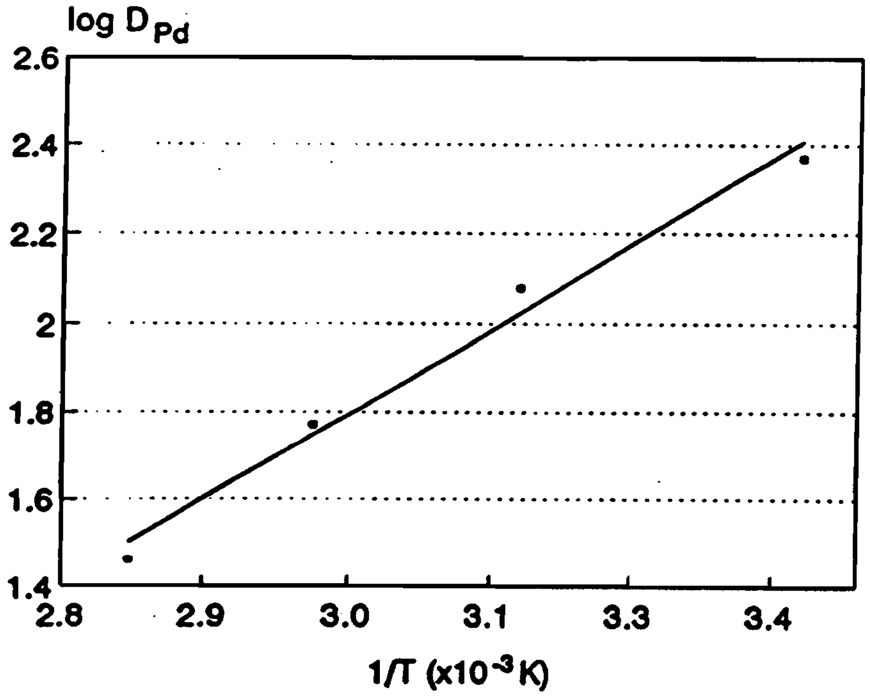

Figure 4.10 Van't Hoff plot for the system Pd(II)-TN 1911-HCl.

4.4.6.2 Extraction Isotherms

In order to evaluate the number of countercurrent stages needed to quantitatively extract Pd(II), extraction isotherms with TN 1911 and TN 2336 were determined and the corresponding McCabe-Thiele diagrams were constructed for A/O=1 (Figure 4.11) [see also Figure B.3 in Appendix B]. Once more, the superior performance of TN 2336 *vis-à-vis* TN 1911 is evident.

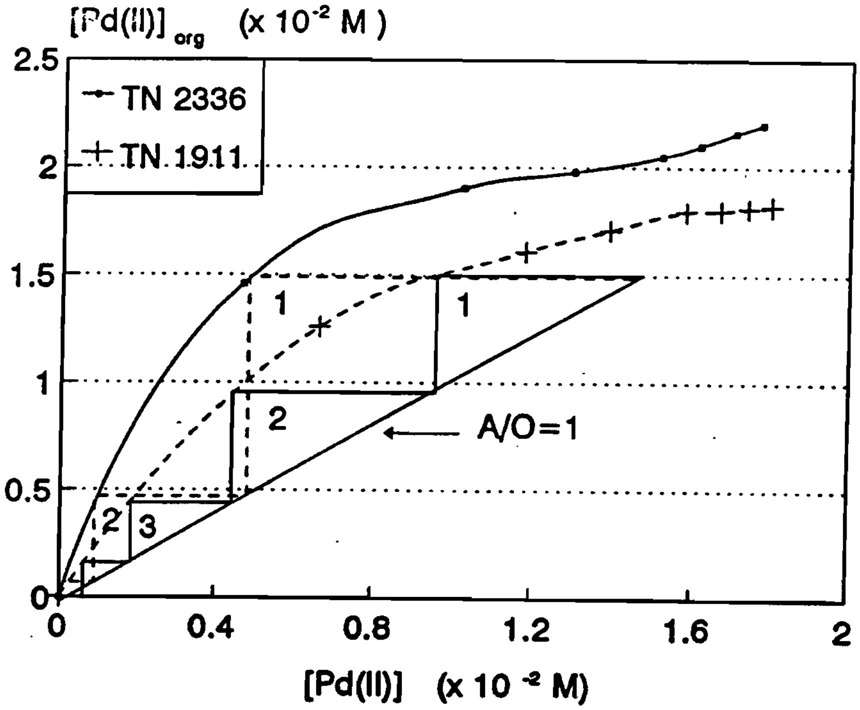

Figure 4.11 Palladium extraction isotherms and McCabe-Thiele diagram CT=15 minutes.

4.4.6.3 Parameters that Influence Pd(II) Stripping

The Acidity of the Stripping Agent

Typical stripping results of Pd-loaded 7-substituted 8-hydroxyquinoline extractants are shown in Figure 4.12. The results were compiled using the cross-current stripping procedure, i.e. the same organic phase was contacted several times with fresh portions of stripping solution. Almost fully loaded extractants (TN

1911 and TN 2336), and two stripping media, 5.1 and 8.0M HCl, were used respectively. The contact time was three minutes and the A/O=1 was kept constant in each contact. The results suggest superior stripping performance by TN 1911 than TN 2336 which is in agreement with the extraction data shown in Figure 4.5. However, Figure 4.12 shows that as the acidity of the stripping agent increases, the overall stripping efficiency for both reagents decreases. There are two possible causes for this behaviour. On one hand, it is likely that part of palladium is retained in the organic phase. Reaction 4.5 describes the possible ion-pair retention mechanism.

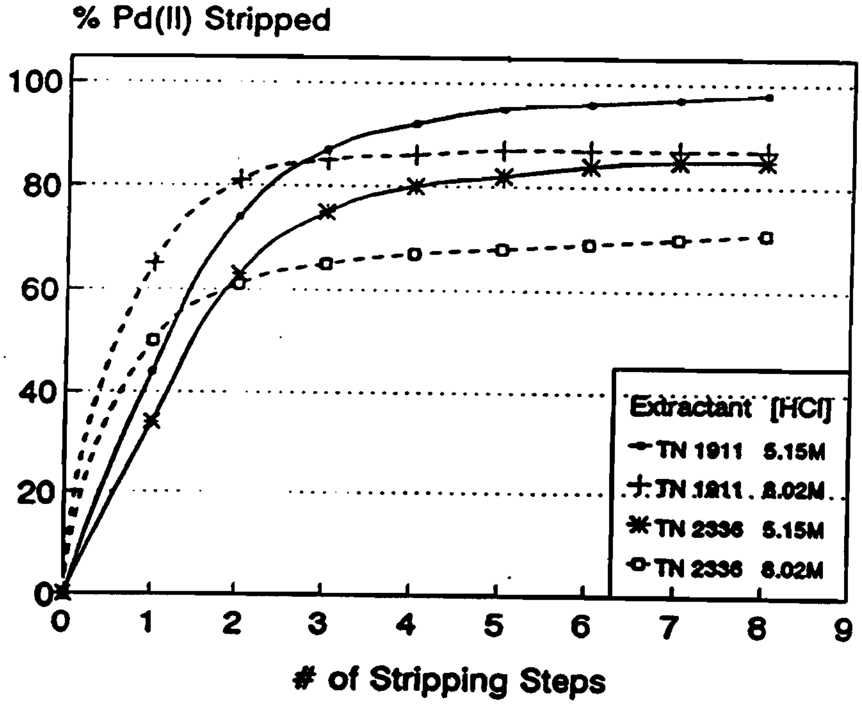

Figure 4.12 Stripping of palladium with 5.15 and 8.05M HCl as a function of consecutives stripping steps CT 3 min.

$$PdCl_4^{2-} + 2H_2Q^+Cl^-_{org} \rightleftarrows (H_2Q^+)_2.PdCl_4^{2-}{}_{org} + 2Cl^- \qquad (4.5)$$

However, such retention (assuming a reversible reaction) was not noted with the extraction results presented in Figure 4.7 showing a monotonous decrease of palladium extraction as a function of feed acidity. On the other hand, stripping tests involving 30 minutes contact time [see the next section] proved that complete removal of palladium by 8.0M HCl is possible. This suggests then, that the observed retention of palladium in the organic phase (Figure 4.12) is not related to a competitive ion-pair extraction mechanism as shown in reaction 4.5, but rather is of kinetic origin. The kinetics of Pd(II) extraction and stripping is currently under investigation in our laboratory. [The results are presented in Chapter 6.]

The Addition of $MgCl_2$ in the Stripping Agent

It is known that addition of $MgCl_2$ strongly increases the activity of hydrogen ion in solution while the activity of chloride ion remains almost constant (23). Therefore, solutions of 4.11M HCl mixed with $MgCl_2$, [see Figure B.6] in concentrations ranging from 0.50 to 2.00M, were tested in order to evaluate the effect of magnesium chloride with respect to palladium stripping. Figure 4.13 shows the stripping efficiency of TN 1911. Similar results were observed with TN 2336 as well [see Figure. B.7]. These tests were performed in a cross-current fashion. From this figure, it becomes apparent that addition of $MgCl_2$ increases palladium stripping and reduces the number of stages needed to quantitatively recover the metal. Stripping of palladium with a mixed HCl/$MgCl_2$ medium is therefore equivalent to or better than with HCl alone.

Finally, the apparent difference in stripping efficiency observed with the 8.0M HCl media (Figures 4.12 versus Figure 4.13) is tentatively attributed to kinetic factors as it was already mentioned in the previous section.

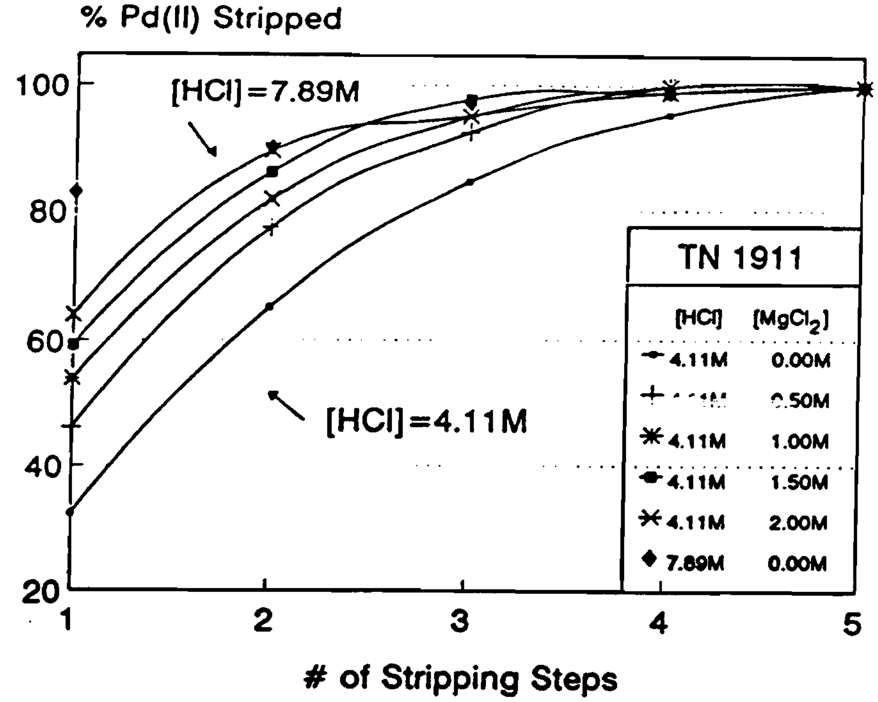

Figure 4.13 Stripping of palladium by 7.89M HCl and 4.11M HCl/0-2.00M $MgCl_2$ as a function of the number of consecutive stripping steps CT 30 min.

4.5 Summary

The extraction equilibria of Pd(II), with chloroform solutions of 7-substituted 8-HQ derivatives, from aqueous chloride media were studied. It was found that $PdCl_4^{2-}$ is extracted, as a simple chelate, PdQ_2, according to the following stoichiometric reaction.

$$PdCl_4^{2-} + 2HQ_{org} \rightleftarrows PdL_{2org} + 2H^+ + 4Cl^-$$

The extraction equilibrium constants, K_{ex}, were determined to be log K_{ex}=5.59 and 5.84 for TN 1911 (an unsaturated and sterically-hindered derivative) and TN 2336 (a saturated and sterically-free derivative) respectively. It was found that PdQ_2

exhibits an absorption band at 460 nm in chloroform.

It was shown that palladium extraction is influenced by both the extractant concentration and reagent structure. The relative importance of the steric effect over the electronic one with respect to metal extraction was discussed. The individual effects of proton and chloride ion concentration on metal extraction were quantified. It was found that palladium extraction is exothermic with an enthalpy change of -29.6 kJ/mol. The effect of stripping agent composition with respect to Pd(II) stripping was discussed. It was found that mixtures of HCl and $MgCl_2$ solutions are superior to simple HCl media.

4.6 Acknowledgements

This research has been generously supported by Schering Berlin AG, the Noranda Technology Centre and The Natural Sciences and Engineering Research Council of Canada.

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Appendix B

Supplement on Pd(II) Extraction Work

As part of the Pd(II) extraction study (the main body of which is reported in chapter 4) the following complementary Figures are presented.

B.1 UV-Visible spectra

In Figure B.1 the UV-Visible spectra of $PdCl_4^{2-}$ in HCl, tridecanol in $CHCl_3$, and Pd-loaded TN 1911 in $CHCl_3$ in the region 200 to 350 nm are shown. The UV-Visible spectra of Pd-loaded TN 1911 in the region 350 to 550 nm for

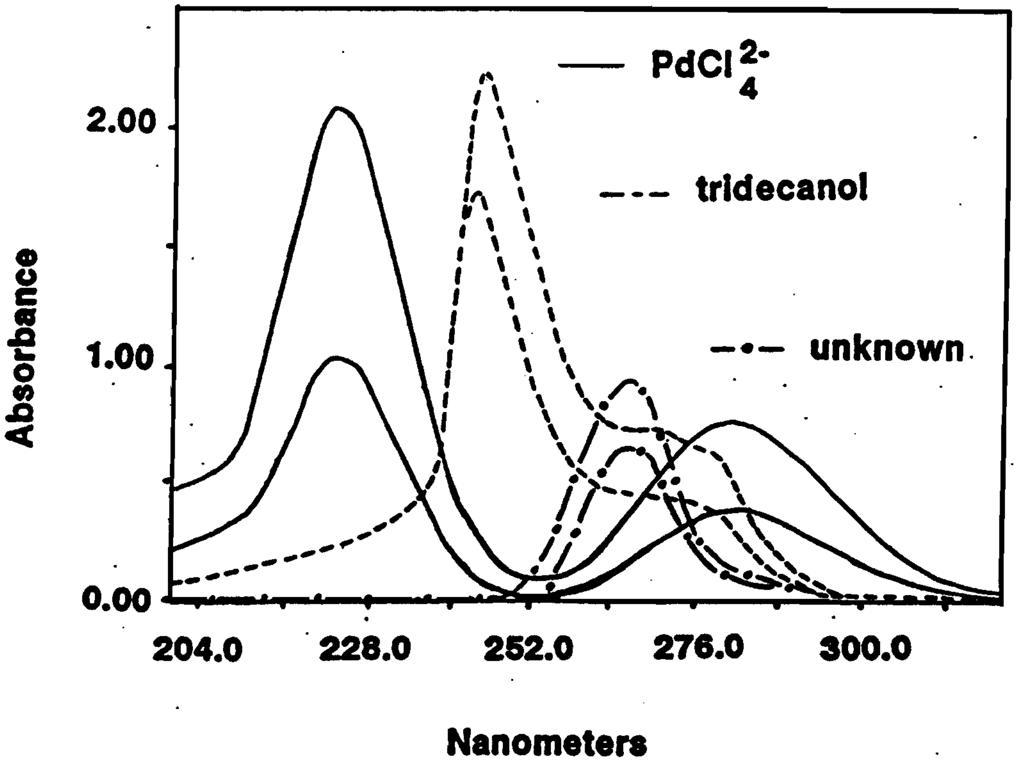

Figure B.1 UV-Visible spectra of $PdCl_4^{2-}$ in HCl, tridecanol and Pd-loaded TN 1911 dissolved in $CHCl_3$ in the region 200-350 nm.

different dilution levels are given in Figure B.2. In Figure B.1 the spectra of $PdCl_4^{2-}$ reported are in agreement with those reported by Elding (8). The UV study of the organic phase after a series of loadings with Pd(II) revealed two absorption bands located at 265.4 nm, (Figure B.1) and 460.0 nm (Figure B.2) respectively. The intensity of the 460.0 nm absorption band increased as the number of loadings was increased. The latter absorption band characterizes the chelate, PdQ_2, formed between TN 1911 or TN 2336 and Pd(II). Similar observation was reported by Al-Bazi and Freiser for the chelate complex formed between Kelex 100 and Pd(II)

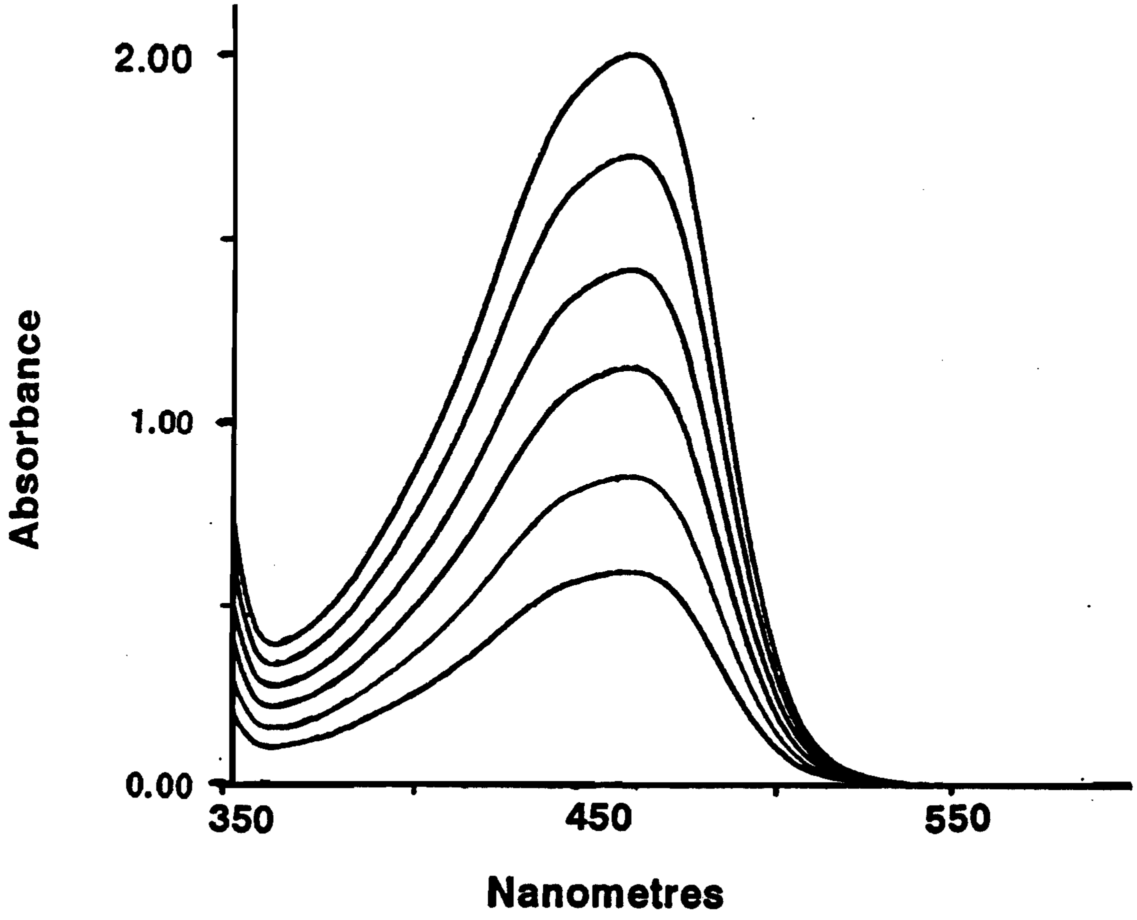

Figure B.2 UV-Visible spectra of PdQ_2 in $CHCl_3$ (TN 1911)

(9). The 265.4 nm band (Figure B.1), whose absorptivity (log ϵ = 5.41) was much larger than that of the 460.0 nm (log ϵ = 3.74), is thought to be due to an impurity or by-product ("unknown" in Figure B.1) present in the organic phase.

B.2 Pd(II) Extraction Isotherms

The extraction curves obtained with the four TN reagents after contacting the two phases for 30 or 15 minutes have been already presented in Figures 4.5 and 4.11 respectively. However, the applied contact time did not allow for the true equilibrium to be reached. Thus, new extraction isotherms were determined using 6 days equilibrium time. The equilibrium isotherms constructed in this way are depicted in Figure B.3. Under equilibrium, both extractants, TN 1911 and TN 2336 exhibit similar loading patterns and very favourable distribution coefficients. It appears, therefore, the better performance of TN 2336 exhibited over TN 1911, when a short contact time was used (Figure 4.11), to be of kinetic origin. The kinetics of Pd(II) extraction disussed in Chapter 6 confirm this observation.

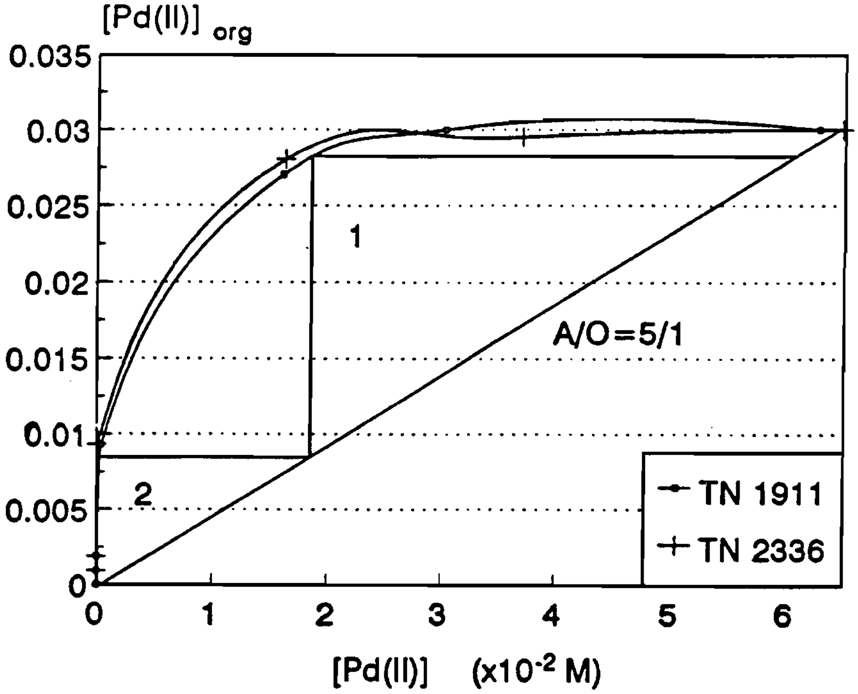

Figure B.3 Equilibrium Pd(II) extraction isotherms and McCabe-Thiele diagram, CT 6 days.

B.3 Pd(II) Stripping Isotherms

Cross-current stripping results of Pd(II) loaded solvents with 5.15M HCl are plotted in Figure B.4. The ease of stripping is according to the stereo-chemical properties of the extractants discussed in Chapter 4. In Figure B.5, Pd(II) stripping isotherms for two different stripping media (i.e. 6.02M HCl and 6.02M HCl + 2.00M $MgCl_2$) and short contact time (3 minutes) are shown. As it is determined in Chapter 6 the rate of stripping is proportional to $[Cl^-]^2$ and this explains the better performance of the HCl/$MgCl_2$ stripping medium with respect to single 6.02M HCl solution. The equilibrium isotherms, for the same stripping solutions, are depicted in Figure B.6. In that case, high volume ratios are seen to be possible. Finally, Figure B.7 shows additionnal stripping results this time for TN 2336.

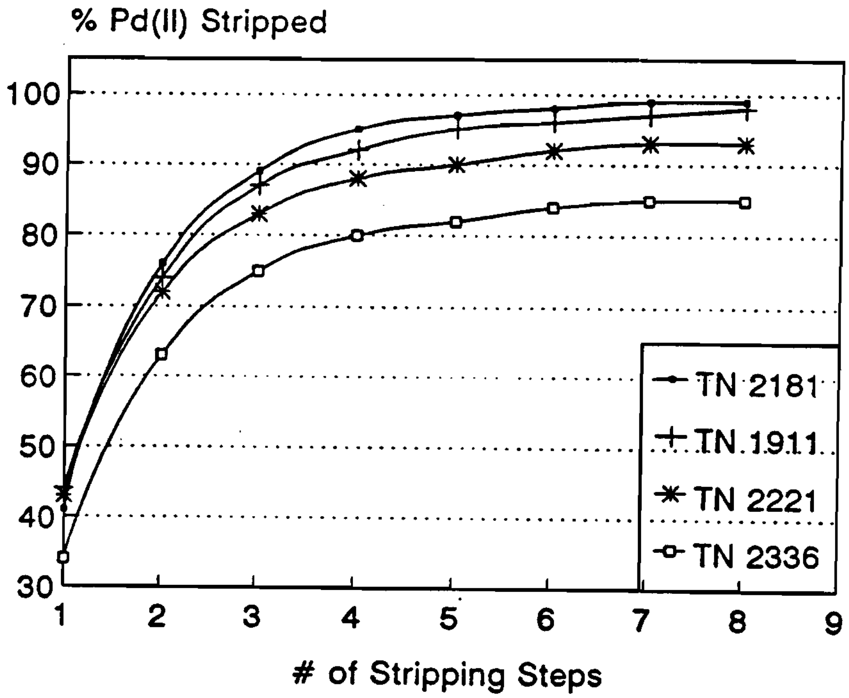

Figure B.4 Stripping of palladium as a function of the number of consecutive stripping steps, CT 3 min.

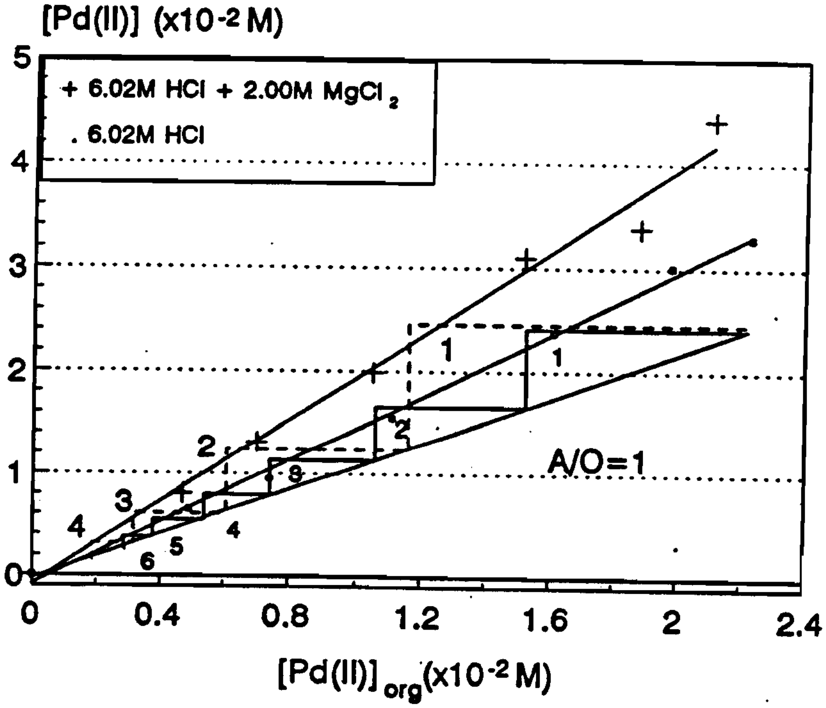

Figure B.5 Palladium stripping isotherms and McCabe-Thiele diagram; stripping agents 6.02M HCl and a mixture 6.02M HCl+2.00M $MgCl_2$, CT 3 min.

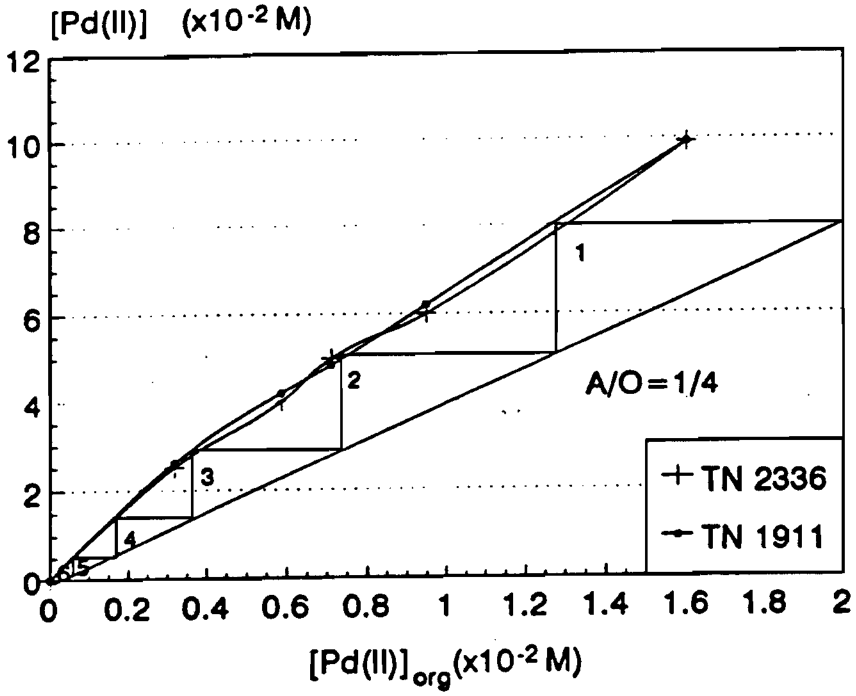

Figure B.6 Equilibrium palladium stripping isotherms and McCabe-Thiele diagram; stripping agents 6.02M HCl and a mixture 6.02M HCl+2.00M $MgCl_2$, CT 6 days.

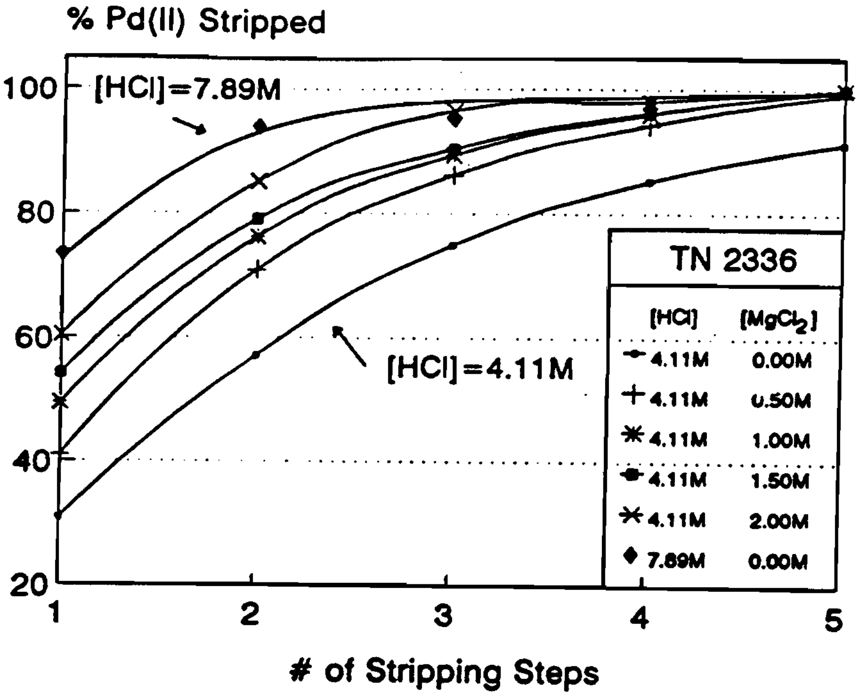

Figure B.7 Stripping of palladium from loaded TN 2336 by 7.89M HCl and 4.11M HCl/0-2.00M $MgCl_2$ as a function of the number of consecutive stripping steps. CT 30 min.

Chapter 5

Pt(IV) Extraction Equilibria and Stripping[1]

5.1 Abstract

Studies of the extraction equilibria of platinum by chloroform solutions of 7-substituted-8-hydroxyquinoline derivatives from aqueous chloride media demonstrated that Pt(IV) is extracted as the ion-pair $PtCl_6^{2-}(H_2Q^+)_2$. The extraction equilibrium constants, log K_{ex}, were determined to be log K_{ex}=3.48 and 3.62 for TN 1911 (an unsaturated and sterically-hindered derivative) and TN 2336 (a saturated and sterically-free derivative) respectively. It was found that $PtCl_6^{2-}(H_2Q^+)_2$ exhibits an absorption band at 254.0 nm in chloroform solution. It was shown that platinum extraction is influenced by both the extractant concentration and reagent structure. The individual roles of platinum, proton and chloride ion concentration were quantified. It was found that platinum extraction is exothermic since metal extraction decreases with temperature and an enthalpy change of -39.8 kJ/mol was determined. The influence of pH on Pt(IV) stripping is also discussed. Finally, the respective extraction and stripping isotherms were established.

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[1] This chapter has been accepted as an article for publication in Solvent Extraction and Ion Exchange, 12(3), (1994). Reprinted by courtesy of Marcel Dekker inc.

5.2 Introduction

In part 1 of this series of publications (1) [Chapter 3], the present authors have reported on the characterization of a number of newly synthesised 7-mono-substituted alkyl or alkenyl derivatives of 8-hydroxyquinoline (8-HQ). These extractants, proprietary products of Schering Berlin AG, Bergkamen, Germany, are labelled: TN 1911, TN 2181, TN 2221 and TN 2336 and have been synthesized specifically for platinum group metal separation. In part 2 (2), [Chapter 4] the fundamental separation chemistry of Pd(II) with 8-hydroxyquinoline derivatives in the 8-HQ-HCl-$MgCl_2$ system was reported.

At McGill University, extensive research has been undertaken over the last few years to develop new solvent extraction methods for the separation of platinum group metals, PGM, using alkylated derivatives of 8-HQ as the preferred family of extractants. This research has led to a patented method (3) of separating Pt(IV) from Pd(II) via co-extraction and differential stripping. Among the commercial reagents which have been tested were Kelex 100 (4), Lix 26 (5) and TN 1911 (6).

The objective of this communication is to describe the fundamental chemistry of separation of Pt(IV) in HCl media with 8-hydroxyquinoline derivatives.

5.3 Experimental

In this investigation, four 8-hydroxyquinoline extractants were used, namely TN 1911, TN 2181, TN 2221 and TN 2336. All 8-HQ reagents were supplied by Schering Berlin AG, Bergkamen, Germany.

Purification of the "as received" extractants consisted of contacting a 0.30M solution of the extractant with an equal volume of 1.42M HCl for 3 consecutive times. This was followed by several washings with equal volumes of water until no chloride was detected in the wash water.

In most of the cases, the extractants were diluted with Solvesso 150 (a diluent with 97% aromatic content; an Exxon Chemicals product) and tridecanol (Harcros Chemicals, Montreal, Quebec, Canada) was added as a phase modifier. Otherwise, the extractants were diluted in chloroform.

Platinum solutions were prepared from pure metal (Johnson Matthey Co.) via *aqua-regia* digestion followed by evaporation to dryness and redissoluton in HCl. All other reagents used such as NaCl, NaOH and various acids, were of reagent grade.

The experimental procedure followed was exactly the same as in part 2 (2) [Chapter 4]. The only difference was that in the present study a 30 minute contact time in conjunction with the slope analysis tests was used as it was found to be more than adequate for reaching equilibrium. Moreover, in the same test the nominal ionic strength was kept constant at 4.00M instead of 2.00M (2) using again the same electrolyte mixtures, i.e. HCl + NaCl and HCl + H_2SO_4.

5.4 Results and Discussion

Similar to part 2 (2) [Chapter 4], two types of experiments were conducted: first, those involving chloroform solutions of the 8-HQ derivatives and second those which involved solutions of 8-HQ in tridecanol-Solvesso 150.

5.4.1 Reagent Characterization

The key features of the various 8-HQ derivatives used are summarized in Table 5.1. In general, the side chains present in these extractants are C_{10}-C_{13}. The latter ones can be either normal or branched. It was found that these extractants were a mixture of various isomers; the exact type of side chain present has already been discussed in part 1 (1) [Chapter 3]. For more information on the characterization of these reagents the reader is also referred to part 2 (2) [Chapter 4] of this series of articles.

Table 5.1 Some features of 8-HQ derivatives

	R Group (1)				Steric Hindrance	
Reagent	Sat	Unsat	# Carbon	Isomer	Low	High
TN 1911		X	10-13	Y		X
TN 2181		X	10-13	?	X	
TN 2221	X		10-13	?		X
TN 2336	X		10-13	?	X	
Kelex 100	X		11	N	(2)	

(1) The abbreviations "sat" and "unsat" refer to saturated and unsaturated R group respectively. (2) medium steric hindrance

5.4.2 The Pt(IV)-HCl-8-HQ-Chloroform System

5.4.2.1 The Stoichiometry of the Extraction of Pt(IV) with 8-HQ Derivatives

Analogies between the behaviour of amines in solvent extraction (SX) systems and the ion exchange technique allow for a better understanding of the behaviour of 8-HQ derivatives as ion-pair extracting reagents. It is known that amines extract hydrochloric acid and metal via an anion exchange process leading to the formation of ion-pairs. Similar behaviour was found for 8-HQ derivatives (1) [Chapter 3].

The equilibrium distribution coefficient of Pt(IV), D_{Pt}, was measured in chloroform solutions of 8-HQ derivatives over the following conditions: [Pt(IV)] ranging from 5×10^{-3} to 2×10^{-3} M, [TN 1911] and [TN 2336] ranging from 2×10^{-2} to 2×10^{-1} M, [H^+] ranging from 2.0 to 4.0 M and [Cl^-] ranging from 2.0 to 4.0 M. The [H^+] range corresponds to the region of full protonation of the extractant (1) [Chapter 3]. In other words, all extractant was present in its protonated form as $H_2Q^+Cl^-$. The speciation diagram of the extractant as a function of HCl concentration has been reported in part 1 (1) [Chapter 3]. This acid range was selected to avoid complications by the existence of both forms of the extractant i.e. the protonated and unprotonated species.

Figures 5.1 to 5.3 show the effect of $[H_2Q^+Cl^-]$, $[H^+]$ and $[Cl^-]$ respectively on D_{Pt}. The plotted data points lie on straight lines of slope 2.02±0.05, -0.16 ±0.03 and -1.89±0.09 for TN 1911 and 2.0±0.1, -0.18±0.06 and -1.8±0.2 for TN 2336 respectively. Also, $[PtCl_6^{2-}]$ in the feed was found not to have any effect on D_{Pt}. This was so since a large excess of extractant was used to perform the slope analysis tests. From Figure 5.2 it can be seen that platinum extraction is independent of proton concentration in the region illustrated in this Figure. This is expected since in this relatively narrow acid region the extractant is fully protonated. The reader is referred to Figure 5.6 later in this paper for the effect of HCl concentration throughout the whole acid range.

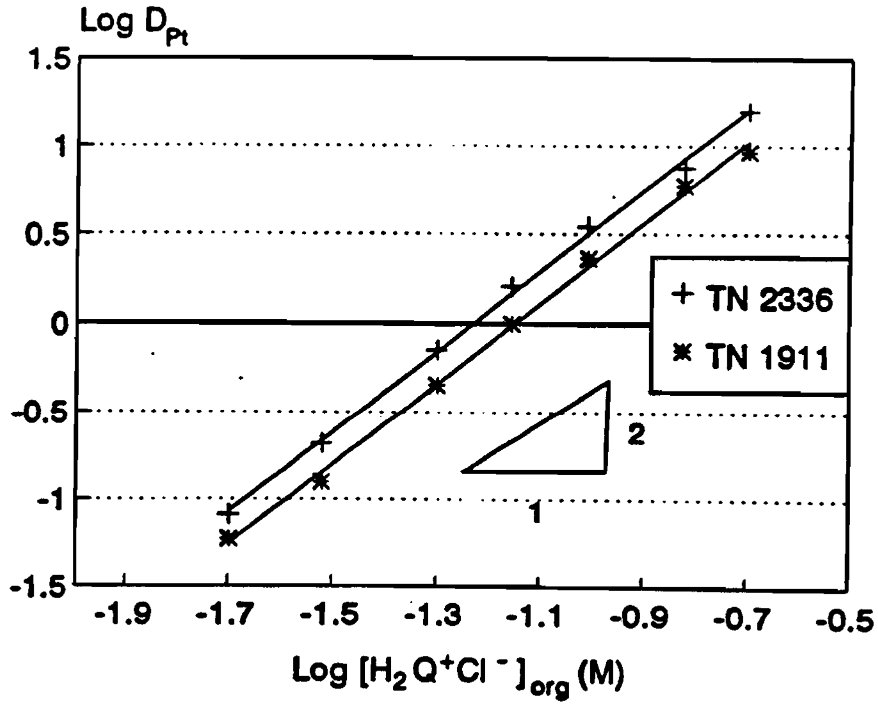

Figure 5.1 Log D_{Pt} as a function of log[protonated extractant]$_{org}$

Figure 5.3 shows that Pt(IV) extraction is suppressed at high chloride ion concentrations. Similar observations were reported for TOPO (7). From the dependence of D_{Pt} on the above mentioned parameters, the extraction reaction stoichiometry is deduced to be expressed by the following reaction:

$$PtCl_6^{2-} + 2H_2Q^+Cl^-_{org} \rightleftarrows PtCl_6^{2-}(H_2Q^+)_{2org} + 2Cl^- \qquad (5.1)$$

The subscript "org" denotes species in the organic phase. Consequently, D_{Pt} is expressed as :

$$D_{Pt} = K_{ex}[H_2Q^+Cl^-]^2_{org} / [Cl^-]^2 \qquad (5.2)$$

The values of extraction equilibrium constant (K_{ex}) were calculated from the following equation:

$$\log K_{ex} = \log D_{Pd} - 2\log [H_2Q^+Cl^-]_{org} + 2\log[Cl^-] \qquad (5.3)$$

assuming that $PtCl_6^{2-}$ was the predominant species present in the aqueous phase. The predominance of $PtCl_6^{2-}$, where $[Cl^-]$ is equal or greater to 3.0 M, has been demonstrated by Blasius et al. (8). The log K_{ex} values calculated for TN 1911 and TN 2336 are presented in Table 5.2 along with other extraction equilibrium constants for other extractants. Judging from the magnitude of the log K_{ex} values, the 8-HQ derivatives are seen to be weaker than the common tertiary amine, TOA (log K_{ex}=6.3) (9) and TOPO (log K_{ex}=5.3) (10).

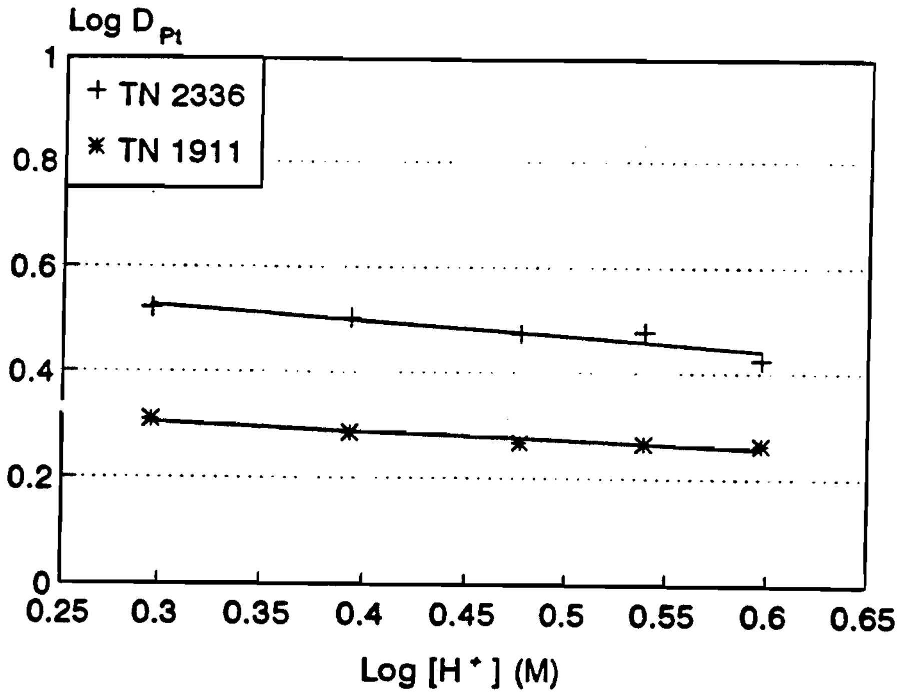

Figure 5.2 Log D_{Pt} as a function of log [H$^+$].

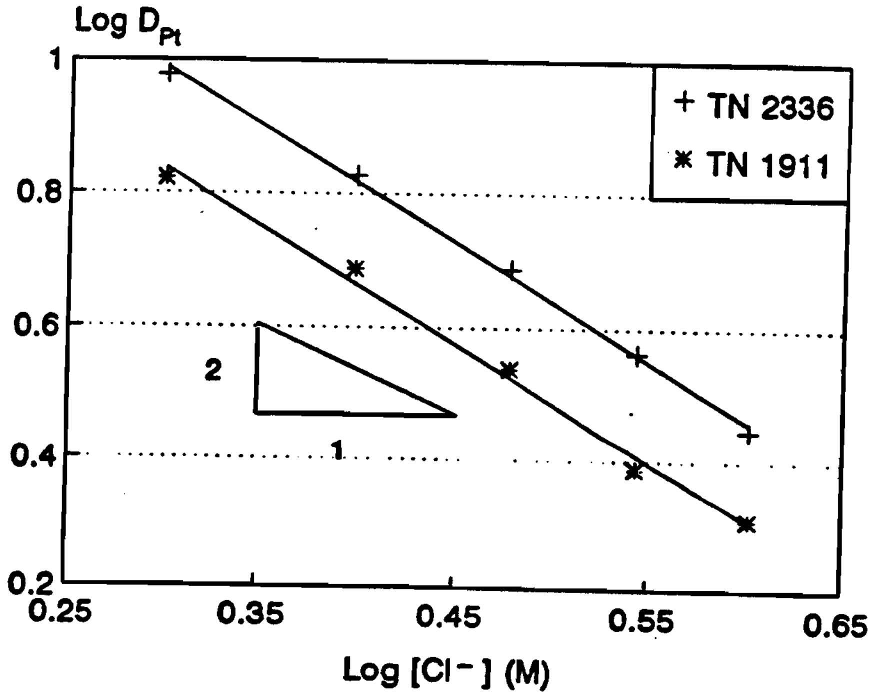

Figure 5.3 Log D_{Pt} as a function of log [Cl$^-$].

Table 5.2 Log K_{ex} values of $PtCl_6^{2-}$ with various extractants

Extractant	Mechanism	log K_{ex}	Ref.
<u>8-HQ</u>			
TN 1911	Ion-pair	3.48±0.06	this study
TN 2663	Ion-pair	3.62±0.06	this study
<u>Amines</u>			
TOA	Ion-pair	6.3	9
<u>Phosphine Oxide</u>			
TOPO	Ion-pair	3.55	10
TOPO	Ion-pair	5.3	9

The abbreviations in Table 5.2 are the following: TOA; tri-n-octylamine and TOPO; trioctylphosphine oxide.

Some clarification is required here with reference to the two log K_{ex} values reported in literature for TOPO. The significant difference between the two reported values does not seem to come from the experimental procedure followed by the two groups of researchers (9,10) but rather from the respective method applied to data treatment. Thus, Hasegawa et al. (9) used a conventional approach where the dependence of D_{Pt} was examined as a function of concentration expressed in mole per litre, whereas Inoue et al. (10) have examined the dependence of D_{Pt} as a function of mean HCl activity and/or single proton activity. Moreover, Inoue et al. (10) did not take into account the extraction of acid by TOPO. For these reasons, the value reported by Inoue et al. (10) cannot be directly compared to the log K_{ex} reported by the presents authors. In conclusion, therefore, 8-HQ is a weaker anion exchanging extractant for $PtCl_6^{2-}$ than TOA and TOPO and in this respect possesses a higher selectivity potential.

5.4.2.2 Spectroscopic Characterization

UV-Visible Characterization

UV-Visible spectra of $PtCl_6^{2-}$ in HCl solution were recorded. [These are presented as stack plots in Appendix C.] Differential UV-Visible spectra of 8-HQ derivatives (1) [Chapter 3] and tridecanol (2) [Chapter 4], in chloroform, have already been published. In general, the maximum absorption wavelength of all 8-HQ derivatives was located at about 248.0 nm. Finally, pure solutions of tridecanol in chloroform as reported in part 2 (2) [Chapter 4] was found to display an absorption band at 243.9 nm.

The spectrum of $PtCl_6^{2-}$ [shown in Appendix C] exhibits two absorption bands located at 208.6 and 262.3 nm respectively. These absorbance values are in good agreement with those reported by Jorgenson (11) who has studied platinum speciation in HCl media.

Chloroform solutions of TN 1911 and tridecanol were successively contacted with several portions of fresh Pt(IV) solutions. A UV study of the organic phase after each loading displayed an absorption band, located at 245 nm, whose intensity increased as the number of loadings was increased. This absorption band is therefore associated with the ion-pair, $PtCl_6^{2-}(H_2Q^+)_2$, formed between the protonated extractant and the chloroplatinic anion. Similar observations were made for tridecanol solutions upon loading with platinum solution (see Table 5.3). In the case of tridecanol, the maximum wavelength of absorption is located at 244.5 nm. However, the mechanism of association (ion-pair or solvation) of tridecanol with $PtCl_6^{2-}$ or H_2PtCl_6 was not further investigated.

Table 5.3 UV-Visible characteristics of Pt(IV) and organic species in chloroform

Species	log ϵ	λ_{max} (nm)
$PtCl_6^{2-}$	4.37	262.3
HQ (TN 1911)[1]	4.68	248.8
tridecanol	0.39	243.9
$H_2Q^+Cl^-_{org}$	N/A[2]	390.0
tridecanol-$PtCl_6^{2-}{}_{org}$	N/A[2]	244.5
$PtCl_6^{2-}(H_2Q^+)_{2org}$	5.21	245.0

[1] see reference 1 [Chapter 3]; [2] not available

The maximum wavelength of absorption of $PtCl_6^{2-}(H_2Q^+)_2$ is located at almost the same wavelength as the free extractant. In general, the ion-pair maximum wavelength of absorption is close to that of the free and unloaded extractant. Similar observations were made for the system $AuCl_4^-$-Lix 26-isodecanol-Solvesso 150 (12). Lix 26 is another 7-substituted 8-hydroxyquinoline derivative which is commercially available (1) [Chapter 3].

Infrared Characterization

The infrared spectrum of neat TN 1911 has already been published elsewhere (1) [Chapter 3]. The examination of chloroform solutions of TN 1911 and tridecanol contacted several times with fresh portions of $PtCl_6^{2-}$ solution showed that the intensity of the O-H band located at about 3390 cm^{-1} for TN 1911 (1) [Chapter 3] does not change as the amount of Pt(IV) present in the organic phase is increased. Also, the rest of the spectrum of loaded TN 1911 is similar to that of the unloaded one. Similar observations have been reported for other similar ion-pair extraction systems (13,14).

5.4.2.3 The Relationship between Extractant Structure and Pt(IV) Extraction

Figure 5.4 shows comparative extraction data for the various reagents. Here, saturation of the extractants was achieved in a cross-current loading mode, i.e. the same organic phase was contacted several times with fresh portions of feed solution. From Figure 5.4 it can be seen that TN 2336 and TN 2181, the extractants experiencing the weakest steric hindrance (see Table 5.1) extract more platinum than their counterparts -TN 2221 and TN 1911- which exhibit strong steric interference. This behaviour is in accordance with the measured intra-molecular hydrogen bonding described in part 2 (2) [Chapter 4]. Also, the strong extraction ability of TN 2336 in comparison to TN 1911 is in agreement with the findings reported previously by these authors (1) [Chapter 3] that the nitrogen atom of TN 2336 is more basic than that of TN 1911.

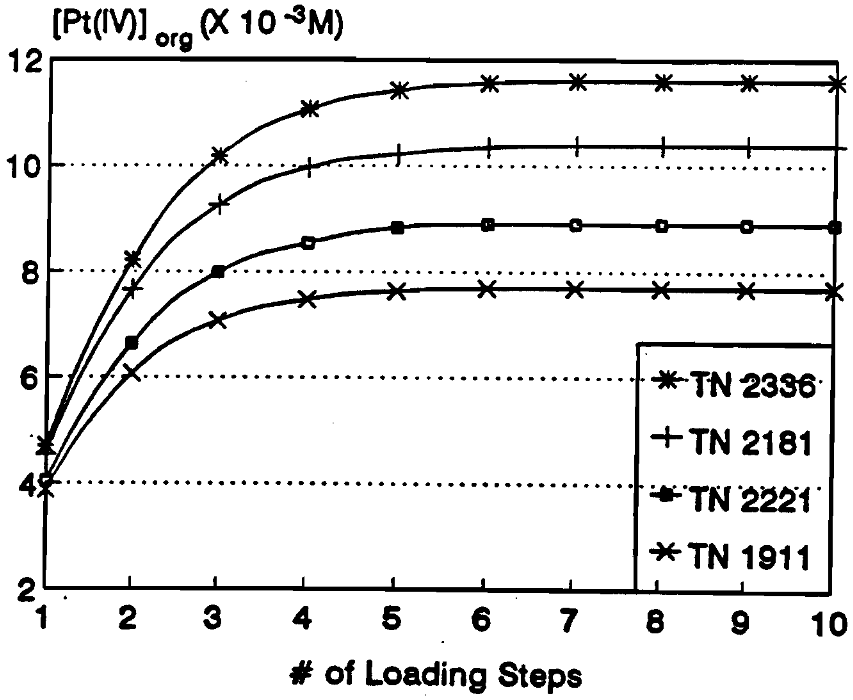

Figure 5.4 Extraction of platinum as a function of the number of consecutive loading steps.

5.4.3 The Pt(IV)-HCl-8-HQ-Tridecanol-Solvesso 150 System

All of the data reported so far, with the exception of Figure 5.4, were collected using chloroform solutions of each of the 7-substituted 8-HQ derivatives investigated. However, industrial solvent extraction does not make use of chloroform and a different formulation must be used. In the case of PGM extraction with commercial 8-HQ extractants, it has already been established (5) that the extractant should be diluted in an aromatic diluent, namely Solvesso 150, along with a long chain alcohol, such as isodecanol or tridecanol, which acts as phase modifier. Thus, in the rest of this paper, the parameters which influence the extraction of Pt(IV) from chloride solutions with 8-HQ derivatives are studied in the Extractant-Tridecanol-Solvesso 150 system.

5.4.3.1 Parameters that Influence Pt(IV) Extraction

The Organic Phase Composition

Figure 5.5 shows that a plot of log D_{Pt} against log $[H_2Q^+Cl^-]$, gives a straight line of slope 2.1 ± 0.1. This agrees well with the corresponding chloroform system (Figure 5.2).

Also, solutions of tridecanol diluted in Solvesso 150 were contacted with Pt(IV) solutions of various acidities (from 1.0 to 7.0 M). It was found that the phase modifier is able to extract Pt(IV) [see Figure C.2 in Appendix C]. Here, a linear relationship between the feed acidity and the amount of metal extracted was observed. However, significant amount of metal [and HCl] starts to be extracted only at a feed acidity greater than 4.00M HCl. Finally, the presence of tridecanol does not have a synergistic effect on Pt(IV) extraction [see Figure C.3 in Appendix 3]. Similar observations have been found in our laboratory for the $AuCl_4^-$-Lix 26-isodecanol-Solvesso 150 system (12).

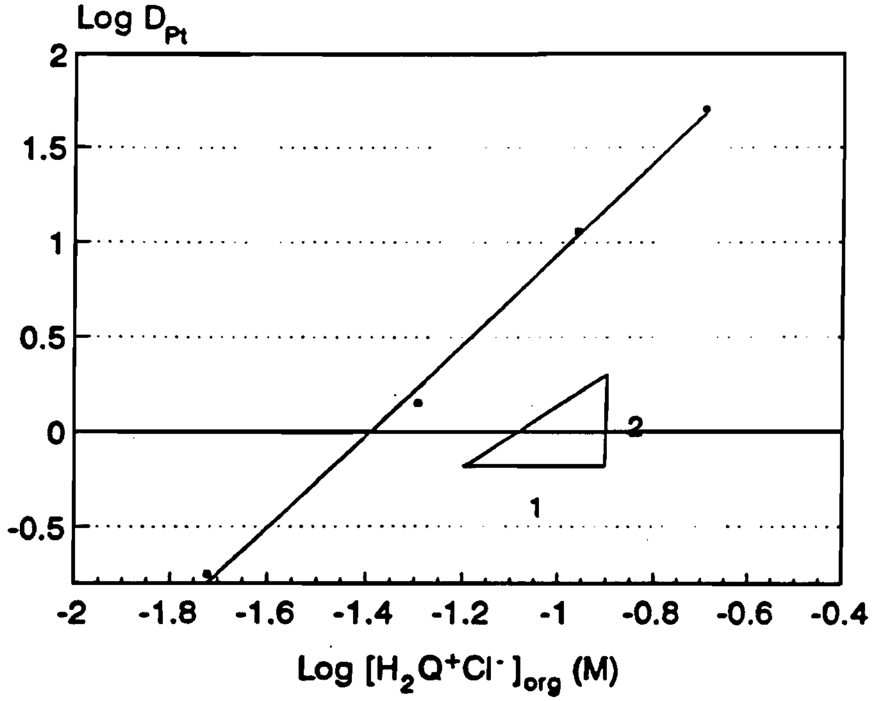

Figure 5.5 Log D_{Pt} as a function of log [protonated extractant]$_{org}$.

The Feed Composition

Similarly to the chloroform system, Figure 5.6 shows that the feed acidity influences the extraction of Pt(IV) for both extractants. As the concentration of HCl in the feed increases three different zones are observed. For [HCl] below 2.0 M, it can be seen that the concentration of Pt(IV) in the organic phase increases accordingly. This proves that as the feed acidity increases, the concentration of the protonated extractant in the organic phase increases as well. The extractant speciation diagram as a function of feed acidity (1) [Chapter 3] is also reploted in Figure 5.6 allowing direct comparison between the Pt(IV) extraction data and the extent of reagent protonation. Also, in the same zone, the efficiency of TN 2336 is greater than that of TN 1911. This is consistent with the fact that the nitrogen atom of TN 2336 is more basic than TN 1911 (1) [Chapter 3]. For [HCl] between 2.0 and 5.0 M the extent of Pt(IV) extraction becomes independent of the feed

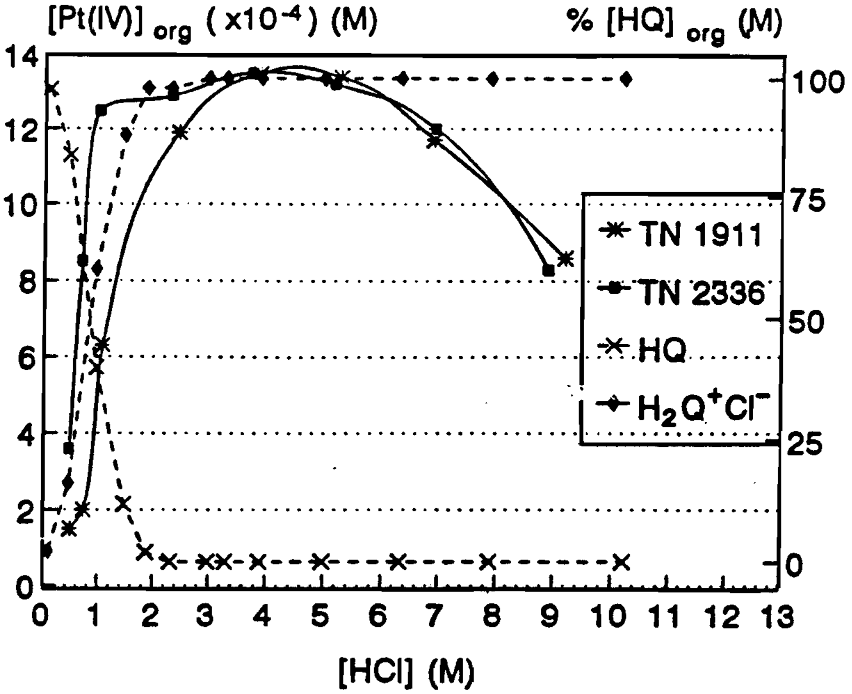

Figure 5.6 Platinum extraction and extractant speciation as a function of [HCl].

acidity. In this acidity range, the concentration of the protonated extractant reaches its maximum and consequently the amount of metal extracted does not increase any further. At [HCl] above 5.0M, Pt(IV) extraction starts decreasing. Various phenomena can account for this case: firstly, the Pt(IV) speciation; at such high HCl concentration H_2PtCl_6 forms in significant amount in the feed (8) thus lowering the platinum extraction and secondly, Le Chatelier's principle readily accounts for the fact that platinum extraction is suppressed by the increased concentration of product, namely Cl^- (reaction 5.1). Alternatively, a further phenomenon responsible for this behaviour maybe the formation of species like HCl_2^- or even $(HCl)_nCl^-$ (n>0) in the aqueous phase (15) which can be extracted preferentially and thus reduce the extraction of Pt(IV).

The individual effect of proton and chloride ion concentration on Pt(IV) extraction with TN 1911 and TN 2336 is depicted in Figure 5.7. The results show

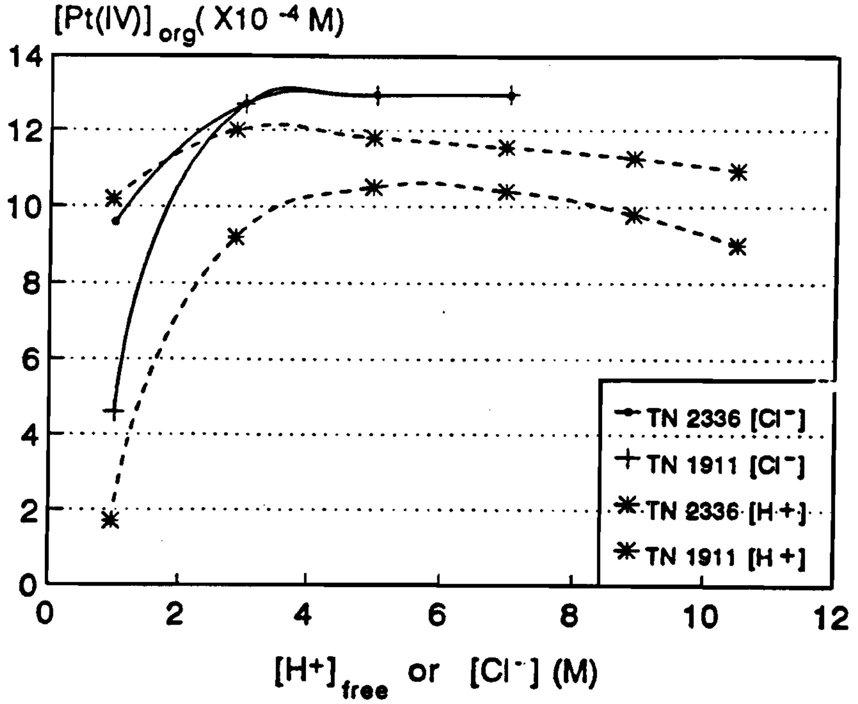

Figure 5.7 Extraction of platinum as a function of [H$^+$] and [Cl$^-$].

that the extent of Pt(IV) extraction increases as the proton or chloride ion concentration increase. The effect of chloride ion, described in Figure 5.7, is slightly stronger than that of proton (the dotted line) on Pt(IV) extraction. The increase of platinum extraction due to chloride addition can be explained from the fact that proton activity is increased by MgCl$_2$ addition (16). This leads to an increase in the concentration of the protonated extractant. On the other hand, a drop in the Pt(IV) extraction at high H$^+$ ion concentration, suggests that H$_2$PtCl$_6^\bullet$ forms and therefore extraction is adversely affected. No such drop was observed with the chloride ion. This might be so because of the lower [Cl$^-$] tested (the maximum [Cl$^-$] was 7.0M) as opposed to 9.0M in the HCl medium of Figure 5.6 and therefore the effect related to Le Chatelier's principle was not clearly manifested.

The Effect of Temperature on Pt(IV) Extraction

The distribution of platinum as a function of temperature and time is presented in Figure 5.8. From this figure, it can be seen that (i) equilibrium is reached within five minutes, (ii) D_{Pt} decreases as the temperature increases. Further treatment of the data presented in Figure 5.8 allowed the estimation of the enthalpy change, ΔH°, for Pt(IV) extraction assuming that Pt(IV) is extracted only according to reaction 5.1. Thus since $[H_2Q^+Cl^-]_{org}$, $[H^+]$ and $[Cl^-]$ were kept constant when the temperature effect was investigated we can use log D_{Pt} in the place of log K_{ex} (Eq. 5.2) and analyze the data with the integrated Van't Hoff equation:

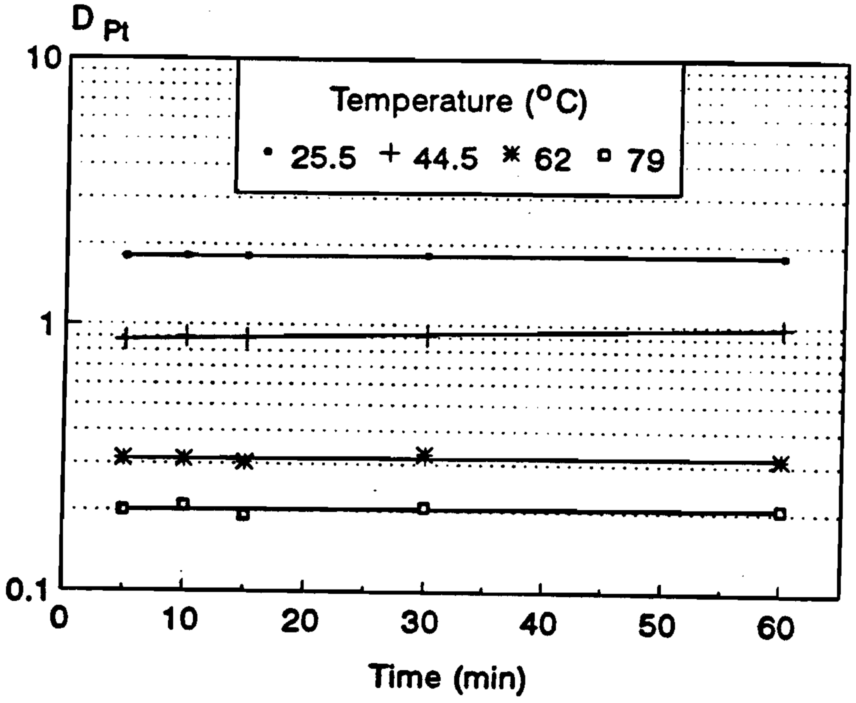

Figure 5.8 Platinum distribution coefficient as a function of temperature and time.

$$\log D_{Pt} = -\Delta H^\circ/2.303RT + \text{constant} \tag{5.4}$$

The Van't Hoff plot is shown in Figure 5.9. From this figure an enthalpy change of -39.8 kJ/mol was determined indicating that the extraction of platinum is exothermic. It is interesting to note that in the equivalent system $AuCl_4^-$-Lix 26-HCl (12) a negative enthalpy change was also found ($\Delta H°$=-58.6 kJ/mol).

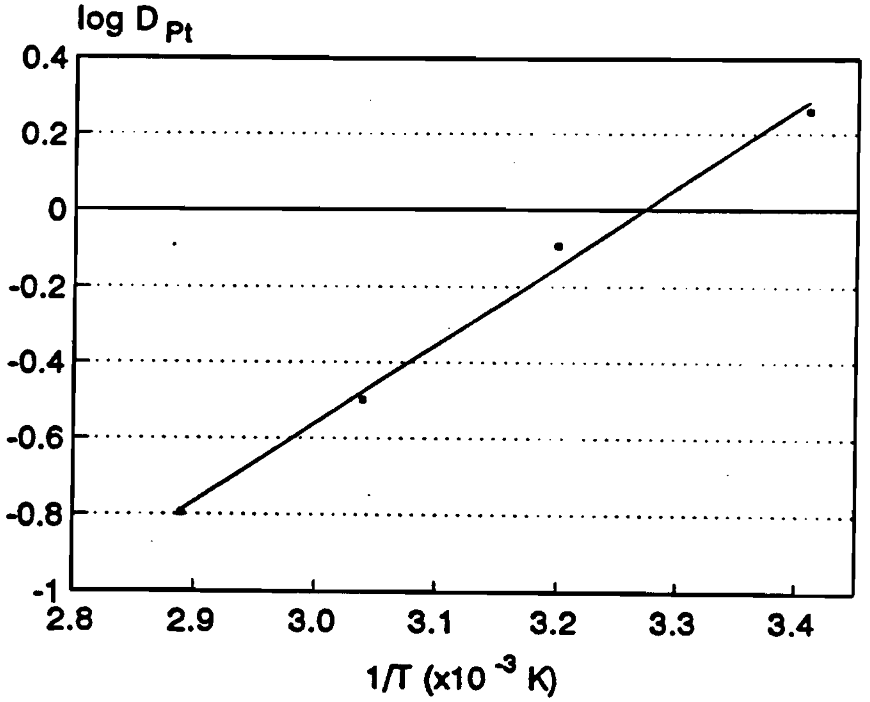

Figure 5.9 Van't Hoff plot for the system Pt(IV)-TN 1911-HCl.

Extraction Isotherms

The excellent Pt(IV) loading characteristics of 8-hydroxyquinoline derivatives are further illustrated with the extraction isotherms of TN 1911 and TN 2336 and the corresponding McCabe-Thiele diagram for A/O=2/1 shown in Figure 5.10.

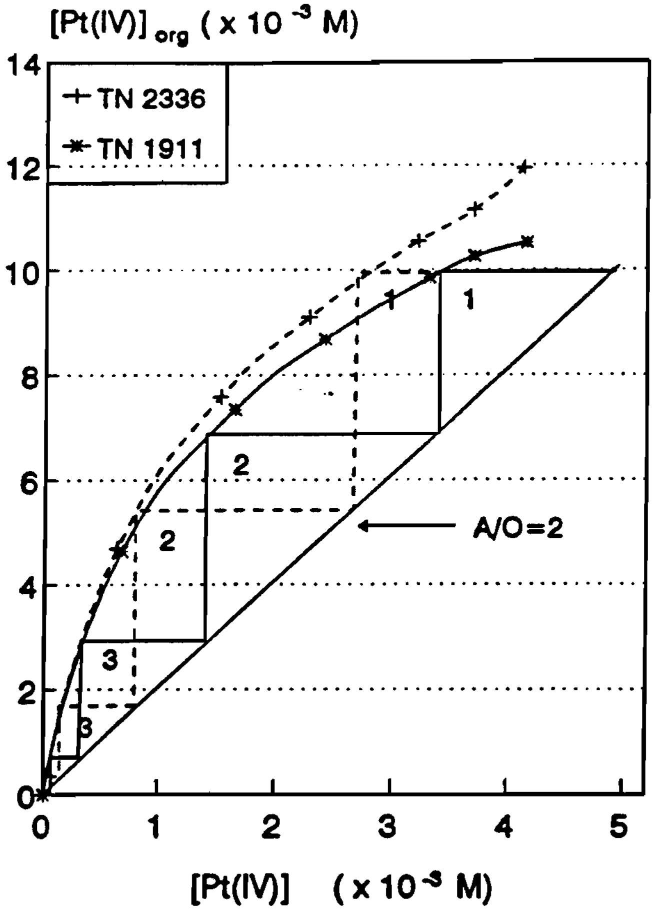

Figure 5.10 Platinum extraction isotherms and McCabe-Thiele diagram.

5.4.3.2 Parameters that Influence Pt(IV) Stripping

Typical stripping results are shown in Figures 5.11 and 5.12. Figure 5.11 shows that a single strip with water is sufficient to strip about 93% of the metal for the given set of conditions at 25 °C. In agreement with the enthalpy of the extraction reaction shown in Figure 5.9, Pt(IV) stripping increases with temperature.

Figure 5.12 shows that as the acidity of the stripping agent decreases, the overall stripping efficiency for both reagents increases. These data also confirm the earlier finding (1) [Chapter 3] that the basicity of TN 2336 is greater than that

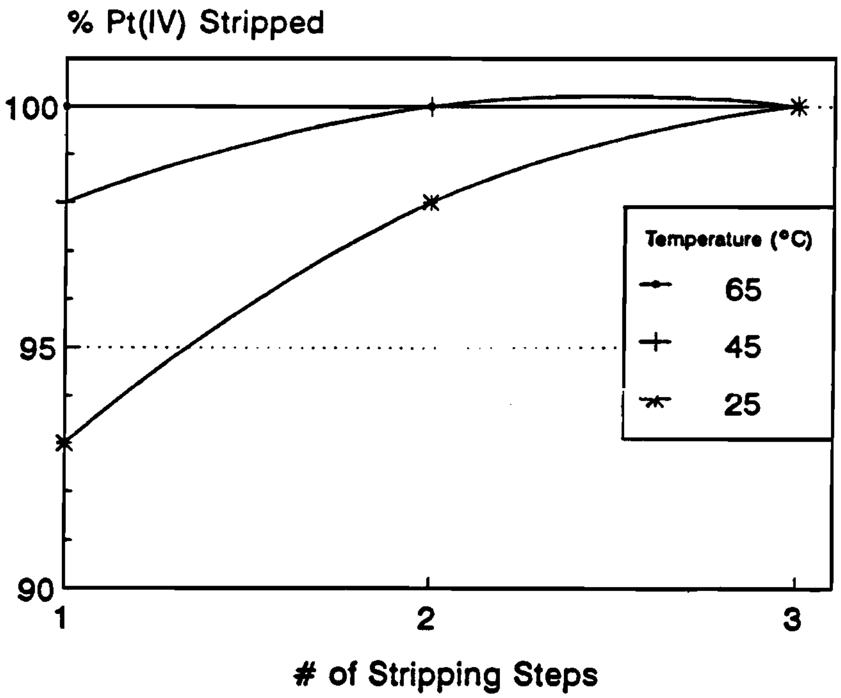

Figure 5.11 Platinum stripped as a function of the number of consecutive stripping steps at various temperatures.

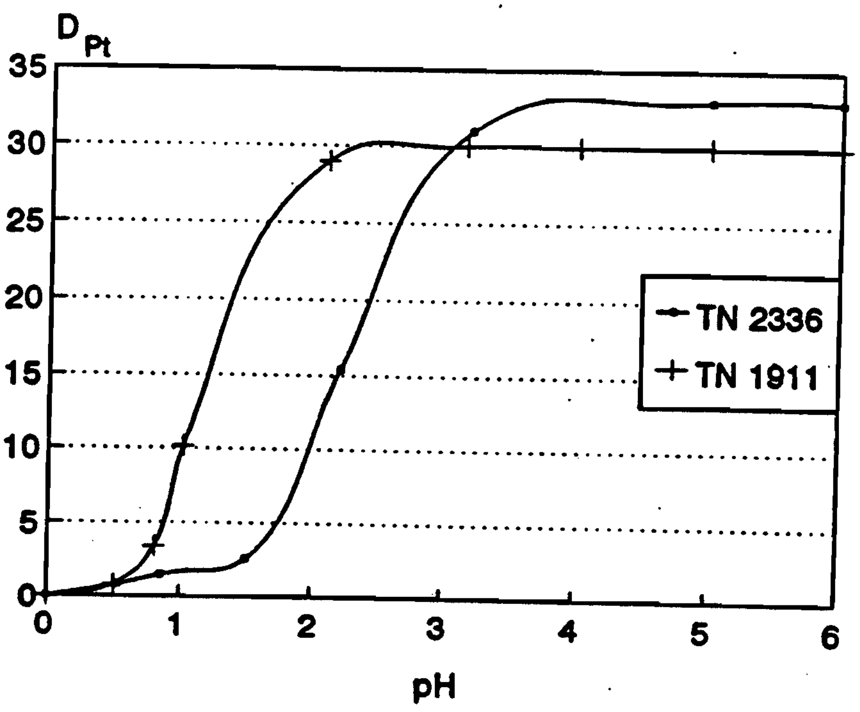

Figure 5.12 Platinum distribution coefficient as a function of pH.

of TN 1911. The order of stripping for the two reagents is exactly the reverse of the extraction order shown in Figure 5.4. Finally, the stripping isotherm of TN 1911 is presented in Figure 5.13.

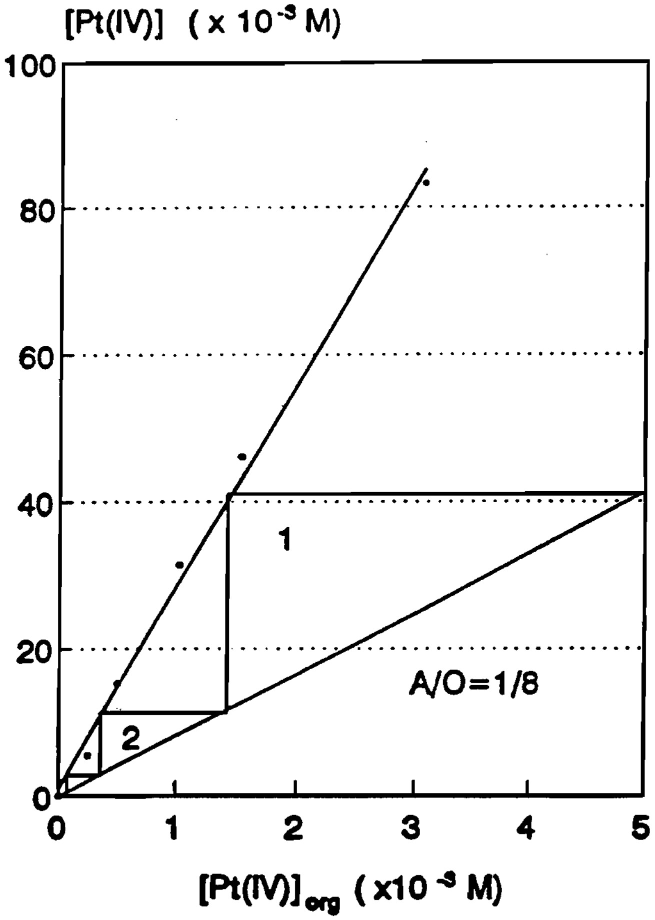

Figure 5.13 Platinum stripping isotherm and McCabe-Thiele diagram.

5.5 Summary

In the present work, the stoichiometric coefficients for the extraction of Pt(IV) with 8-HQ derivatives in chloroform solution from aqueous chloride media have been determined from extraction equilibria. It has been found that $PtCl_6^{2-}$ is extracted as a simple ion-pair, $PtCl_6^{2-}(H_2Q^+)_2$, according to the following stoichiometric reaction:

$$PtCl_6^{2-} + 2H_2Q^+Cl^- \rightleftarrows PtCl_6^{2-}(H_2Q^+)_2 + 2Cl^-$$

The extraction equilibrium constants, log K_{ex}, were determined to be log $K_{ex}=3.48$ and 3.62 for TN 1911 and TN 2336 respectively. By UV spectroscopy, it was found that $PtCl_6^{2-}(H_2Q^+)_2$ exhibits an absorption band at 245.0 nm in chloroform. Tridecanol, the phase modifier, was also found to extract Pt(IV).

It has been shown that platinum extraction is influenced by both the extractant concentration and reagent structure. The sterically-free 8-HQ derivative (TN 2336) was found to extract Pt(IV) at higher distribution coefficients than the respective sterically-hindered one (TN 1911). The individual roles of platinum, proton and chloride ion concentration respectively in the feed solution were determined. It was found that platinum extraction is exothermic with an enthalpy change of -39.8 kJ/mol. Finally, the constructed extraction and stripping isotherms and the very fast kinetics observed showed TN 1911 and TN 2336 to be excellent extractants for Pt(IV).

5.6 Acknowledgements

This research has been generously supported by Schering Berlin AG, the Noranda Technology Centre and the Natural Sciences and Engineering Research Council of Canada (NSERC).

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Appendix C

Supplement on Pt(IV) Extraction Work

As part of the Pt(IV) extraction study (the main body of which is reported in chapter 5) the following complementary Figures are presented.

C.1 UV-Visible spectra

In Figure C.1, the UV-Visible spectra of $PtCl_6^{2-}$ in HCl are depicted.

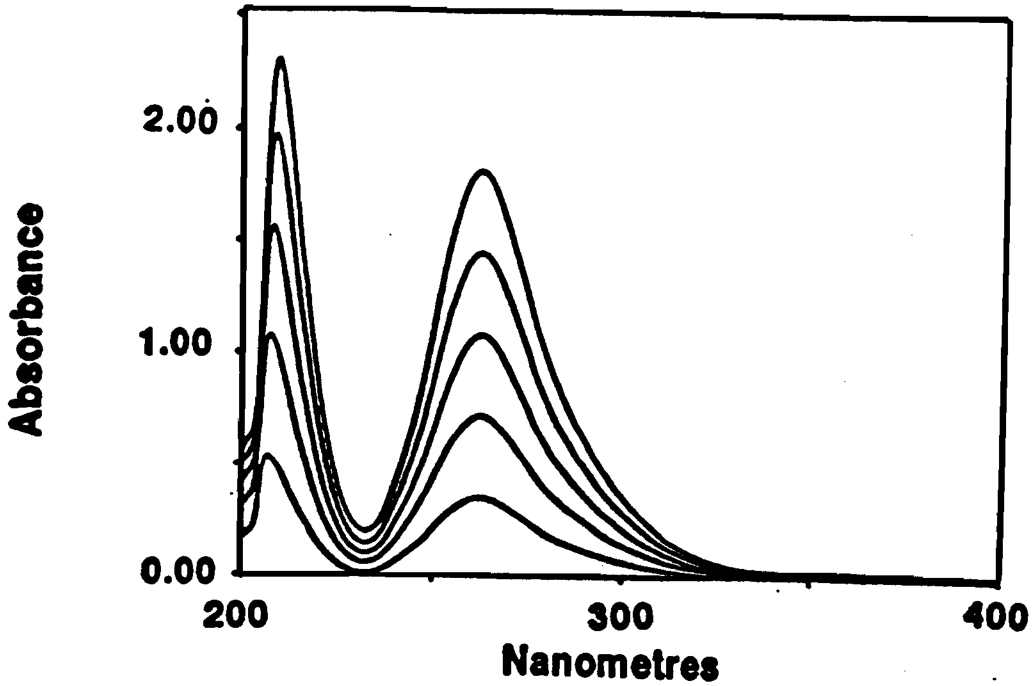

Figure C.1 UV-Visible spectra of $PtCl_6^{2-}$ in 1.52M HCl.

C.2 The effect of phase modifier in the organic phase

In general, the phase modifier plays two roles (a) it improves phase separation, and (b) it increases the solubility of the extracted complex into the organic phase. In the present study, it was found that tridecanol was also able to extract platinum from chloride media.

Figure C.2 displays the ability of pure solutions of tridecanol diluted in Solvesso 150 to extract Pt(IV). It can be seen from this figure that the amount of

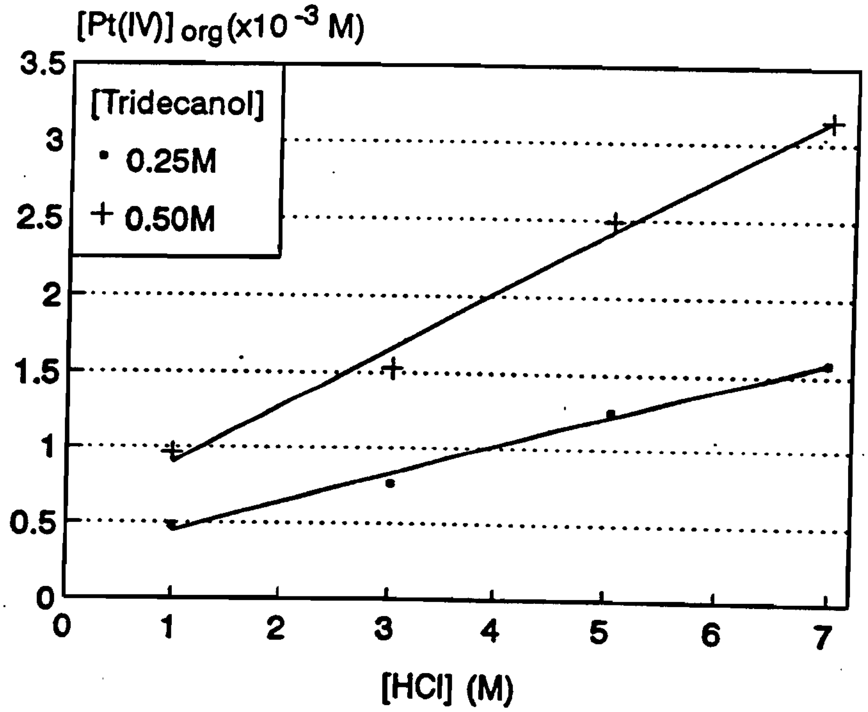

Figure C.2 Extraction of platinum by tridecanol as a function of [HCl].

platinum extracted depends both on (a) the concentration of phase modifier present in the organic phase, and (b) the HCl content of the feed.

Finally, Figure C.3 shows that the presence of tridecanol in the organic phase does not have synergistic effect on metal extraction since both curves are parallel.

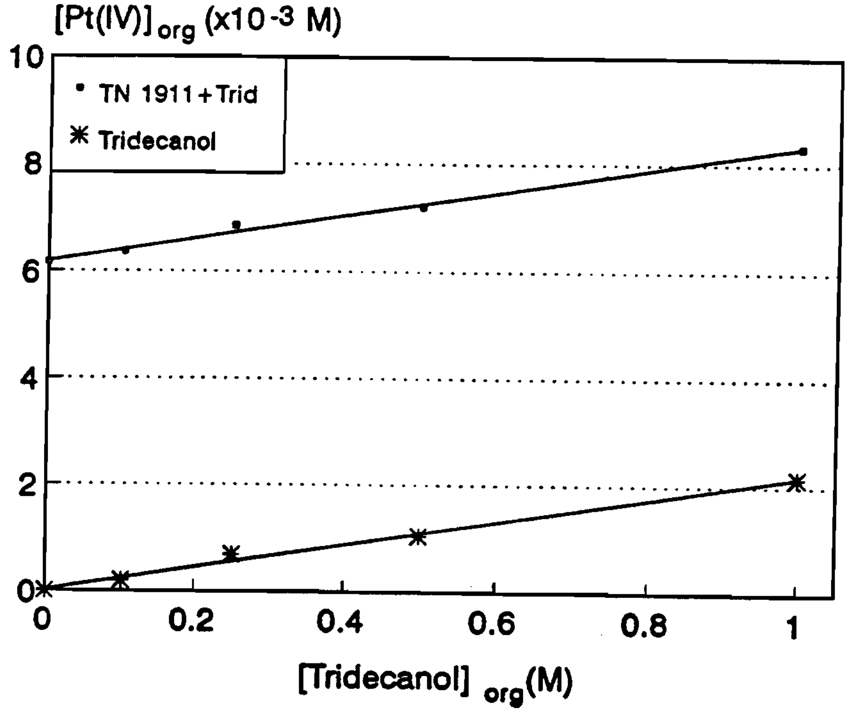

Figure C.3 Extraction of platinum as a function of [Tridecanol]$_{org}$ with and without TN 1911.

Chapter 6

Kinetics of Pd(II) Extraction and Stripping[1]

6.1 Abstract

The extraction and stripping kinetics of Pd(II) by chloroform solutions of 7-substituted-8-hydroxyquinoline derivatives, 8-HQ, (labelled TN 1911, an unsaturated and sterically-hindered derivative, and TN 2336, a saturated and sterically-free derivative) from aqueous chloride media are reported. It is shown the extraction process to go through the fast formation of the ion-pair $PdCl_4^{2-} \cdot (H_2Q^+)_2$ (where H_2Q^+ represents the protonated extractant) and the slow intramolecular transformation of the latter to an inner sphere (chelate) complex. As the slow intramolecular conversion reaction (the postulated rate-limiting step) apparently occurs away from the interface, the extraction reaction was found to be independent of the interfacial area and the agitation speed. The order of the extraction reaction, in the HCl concentration range 0.20-2.00M was found to be 1 with respect to $[PdCl_4^{2-}]$, 0 with respect to $[H^+]$, 2 with respect to $[HQ]_{org}$ and -2 with respect to $[Cl^-]$ for both derivatives. The respective orders for the stripping reaction were 1 for $[PdQ_2]_{org}$, 2 for $[H^+]$ and 2 for $[Cl^-]$ for both extractants again. Pd(II) extraction and stripping rate constants, k_{ext} and k_{strip}, were found to be 0.36 ± 0.05 s^{-1} and 6.8 ± 0.3 $(\times 10^{-6})$ s^{-1} for TN 1911 and 0.6 ± 0.1 s^{-1} and 8.9 ± 0.3 $(\times 10^{-6})$ s^{-1} for TN 2336. It was also observed the presence of Pt(IV) in the organic phase to slow down (although to a modest degree) the extraction rate of Pd(II). It

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[1] This chapter will be submitted as an article for publication in Solvent Extraction and Ion Exchange, (March 1994).

is demonstrated finally that an exchange reaction takes place between Pd(II) and Pt(IV) when the two metals are co-extracted from a mixed metals solution. Thus, Pt(IV) appears to be initially extracted very fast as an ion-pair and then is crowded out by the slowly loading of Pd(II) as chelate in the organic phase.

6.2 Introduction

At McGill University, extensive research has been undertaken over the last few years to develop new solvent extraction methods for the separation of platinum group metals, PGM, using alkylated derivatives of 8-hydroxyquinoline, 8-HQ, as the preferred family of extractants. This research has led to a patented method (1) of separating Pt(IV) from Pd(II) via co-extraction and differential stripping. Among the commercial reagents which have been tested were Kelex 100 (2), later Lix 26 (3) and more recently TN 1911 (4).

This series of articles deals with the fundamental chemistry (equilibria and kinetics) of the Pd(II)-Pt(IV)-HCl-8-HQ solvent extraction system. More specifically, in part 1 of this series of publications (5) [Chapter 3], the present authors have reported on the characterization of several newly synthesised 7-mono-substituted alkyl or alkenyl derivatives of 8-hydroxyquinoline, 8-HQ, and their protonation with HCl. In parts 2 and 3, the equilibria of Pd(II) (6) [Chapter 4] and Pt(IV) (7) [Chapter 5] extraction from single metal chloride solutions with 8-HQ derivatives were reported.

The present communication reports on the kinetics of palladium extraction and stripping from both single and mixed metal (Pd(II)/Pt(IV)) chloride media with two 8-hydroxyquinoline derivatives, namely TN 1911 (a C_{10}-C_{13} unsaturated and sterically-hindered derivative) and TN 2336 (a C_{10}-C_{13} saturated and sterically-free derivative).

6.3 Experimental

The two 8-hydroxyquinoline derivatives used in the present study were development products of Schering Berlin AG, Bergkamen, Germany. Samples of these extractants were generously made available to the authors. The characterization of the "as received" extractants has already been described elsewhere (5,6) [Chapters 3 and 4]. The extractants prior to their use were purified (5) [Chapter 3] by several alternate contacts with 1.42M HCl and water in order to remove solubles impurities. Most of the experiments were conducted with chloroform solutions of the extractants. In a few experiments, the extractants were diluted with Solvesso 150[2] (a commercial diluent with 97% aromatic content) and tridecanol was added as a phase modifier. The latter solvent mixture is the preferred formulation for industrial application (3,4).

All of the tests were performed at 25°C. The majority of the tests were executed in 40 mL vials. Equal volumes (10 mL) of organic and aqueous phases were shaken with a box-type Eberbach shaker at 280 oscillations/minute. The A/O ratio was 1 in all tests. To evaluate the effect of stirring speed a mechanically-agitated reactor was used. The latter was equipped with an impeller and baffles. It must be explained here that a change in the stirring speed (in the given reactor) did not only alter the thickness of the boundary layer, i.e. not only influenced the diffusional rates but also the interfacial A/O area. The reactor diameter and the solution height were 6 and 9 cm respectively. The impeller had a 5.0 cm diameter and it was positioned just below the A/O interface level, i.e. at a height of 4.5 cm.

The aqueous feed solutions were prepared by dissolving Pd or Pt metals in *aqua-regia*, evaporating the solution to dryness and redissolving with HCl. The nominal ionic strength was kept constant at 2.00M or 1.50M respectively using the following electrolyte mixtures: HCl + NaCl or HCl + H_2SO_4.

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[2] proprietary product of Exxon Chemicals

The extraction kinetics were followed via the periodic collection of samples of the raffinate phases (after letting the two phases to separate) and the determination of their decreasing metal concentration by AA spectroscopy. On the other hand, the stripping kinetics were followed by determining directly the concentration of PdQ_2 in the organic phase by UV-Visible spectroscopy at 460 nm (6) [Chapter 4]. The chloroform solution containing the chelate had to be washed at least four times with equal volume of water prior to analysis in order to eliminate the extracted acid and thus destroy the protonated extractant species (5). The latter has a very broad absorption band centered at 390.0 nm which overlaps partially with the absorption band displayed by PdQ_2. UV measurements were done with a Varian Cary 13 UV-Visible spectrophotometer and spectrograde $CHCl_3$ was used as solvent.

For the stripping tests, a saturated organic solution of PdQ_2 was required. This was prepared by contacting the chloroform solution of the extractant (0.01M) several times (CT=30 min) with fresh portions of Pd(II) feed (A/O=1). A similar technique had been used in part 2 (6). For these preparation tests a feed containing 0.01M palladium and 0.05M HCl was used. Under these conditions about five extraction stages were needed to saturate the organic phase with palladium. This saturated chloroform solution was diluted to a known concentration of the chelate and was checked by UV-Visible spectrophotometry prior to its use.

6.4 Results and Discussion

6.4.1 Single Metal Extraction

The overall Pd(II) solvent extraction reaction, the kinetics of which were studied, is the following:

$$PdCl_4^{2-} + 2HQ_{org} \rightleftarrows PdQ_{2org} + 2H^+ + 4Cl^- \qquad (6.1)$$

The stoichiometry of the above reaction has been previously determined with the aid of slope analysis methodology (6) [Chapter 4]. Reaction 6.1 is a reversible one. In order to measure the individual extraction and stripping kinetics it was necessary to isolate the forward, i.e. the extraction from the backward, i.e. the stripping reaction. This was achieved by choosing experimental conditions under which reaction 6.1 was far away from equilibrium. Thus, for the forward reaction a very large excess of extractant was used so the $[HQ]_{org}$ remained almost unchanged. On the other hand for the stripping tests a very large excess of loaded extractant (in comparison to the amount of metal stripped) was used and therefore the $[PdQ_2]_{org}$ remained unchanged.

6.4.2 The Stirring Speed Effect

Before each kinetic parameter was systematically studied, it was verified if the reactor and procedure employed were appropriate for the given reaction system. To this end, first the extraction kinetic measured with the box-type Eberbach shaker (280 osc/min) were compared to that measured with the mechanically-agitated reactor (350 rpm). The obtained results are illustrated in Figure 6.1. As it can be seen, both reactors gave exactly the same $[Pd]_{org}$ as a function of mixing time. Next, the stirring speed effect was studied using the mechanically-agitated reactor. The obtained results presented in the form of $[Pd]_{org}$, after 30 minutes mixing time, as a function of the stirring speed are plotted in Figure 6.2. As it can be seen, the stirring speed had no effect on the kinetics. This implies that the rate limiting step is neither an interfacial diffusional step nor an interfacial reaction step. The latter is said because in the single reactor set up employed, an increase in rpm was unavoidably associated as well with an increase in interfacial area. In other words, the rate limiting step seems to be a homogeneous reaction occurring in either phase, the aqueous or the organic.

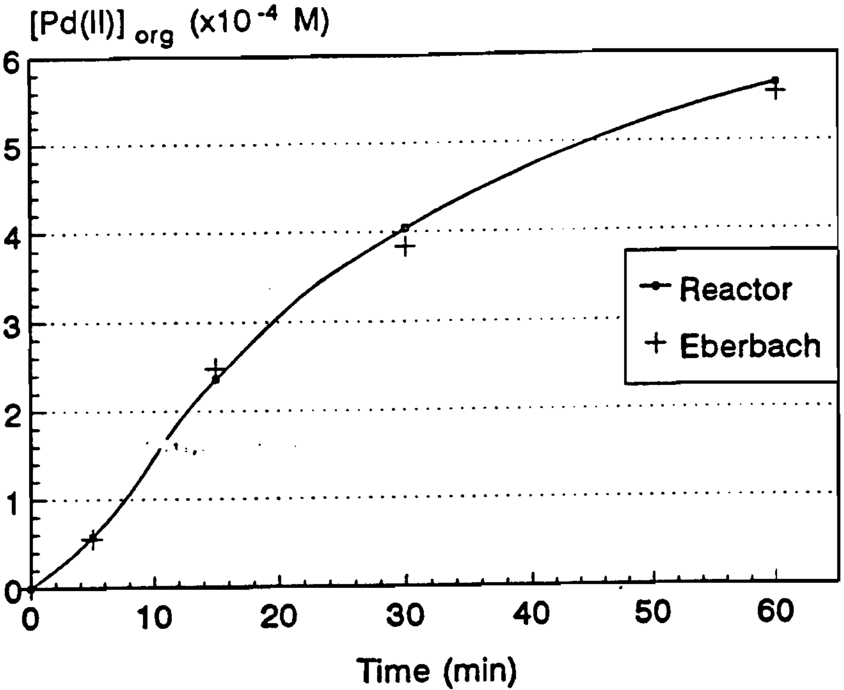


Figure 6.1 Comparison of Pd(II) extraction kinetics measured with two different reactors, a box-type Eberbach shaker (280 osc/min) and a reactor at 350 rpm.

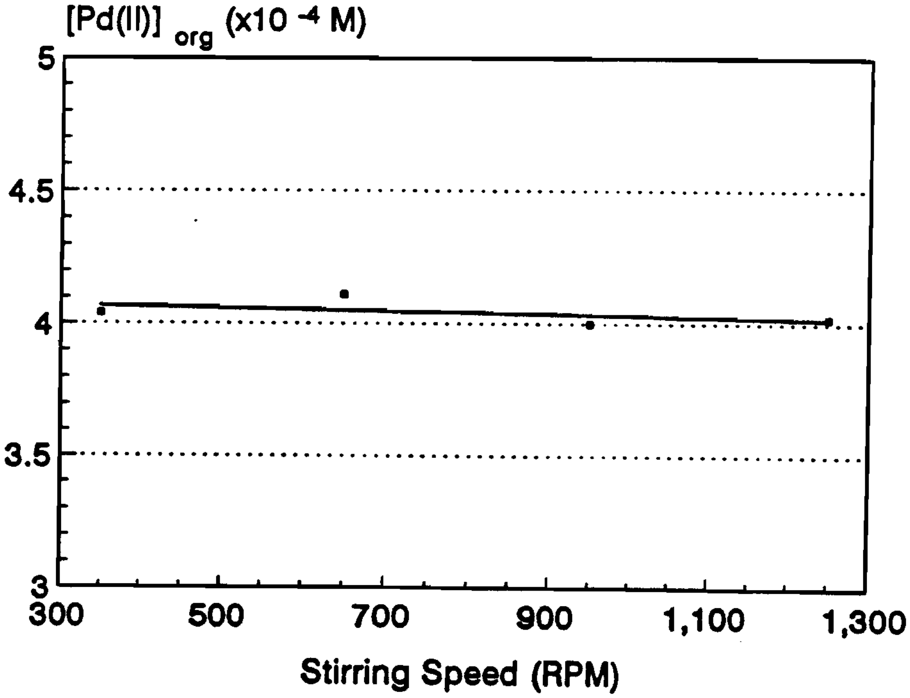


Figure 6.2 The effect of stirring speed on the extraction level of Pd(II) after 30 min. mixing time.

The measured [Pd(II)] versus time data were analyzed with the aid of the integrated first order rate equation:

$$\ln ([PdCl_4^{2-}]_o/[PdCl_4^{2-}]_t) = k_{obs}t \qquad (6.2)$$

Above the subscripts "o" and "t" refer to [Pd(II)] in the aqueous phase at time 0 and time t respectively. All experimental data were found to fit this equation. The first order plots for TN 1911 are shown in Figures 6.3 to 6.5 for various $[H^+]$ (0.20M-2.00M), $[HQ]_{org}$ (5×10^{-3}-3×10^{-2}M) and $[Cl^-]$ (0.20M-2.00M). The respective data for TN 2336 are presented in Table 6.1. The concentrations in brackets refer to the range studied for the given parameter.

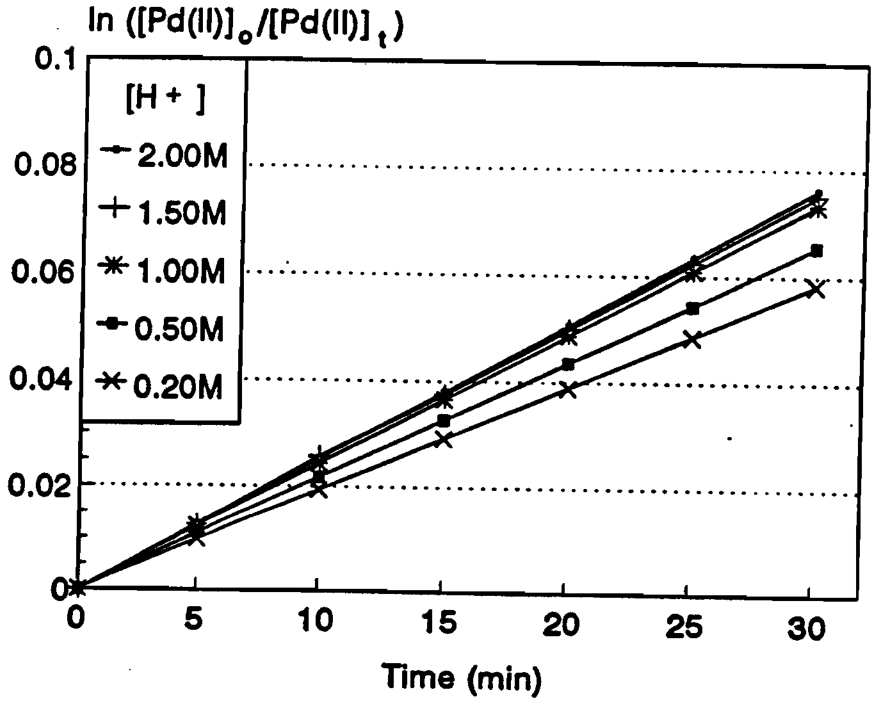


Figure 6.3 First order plots of Pd(II) extraction data at various H^+ concentrations.

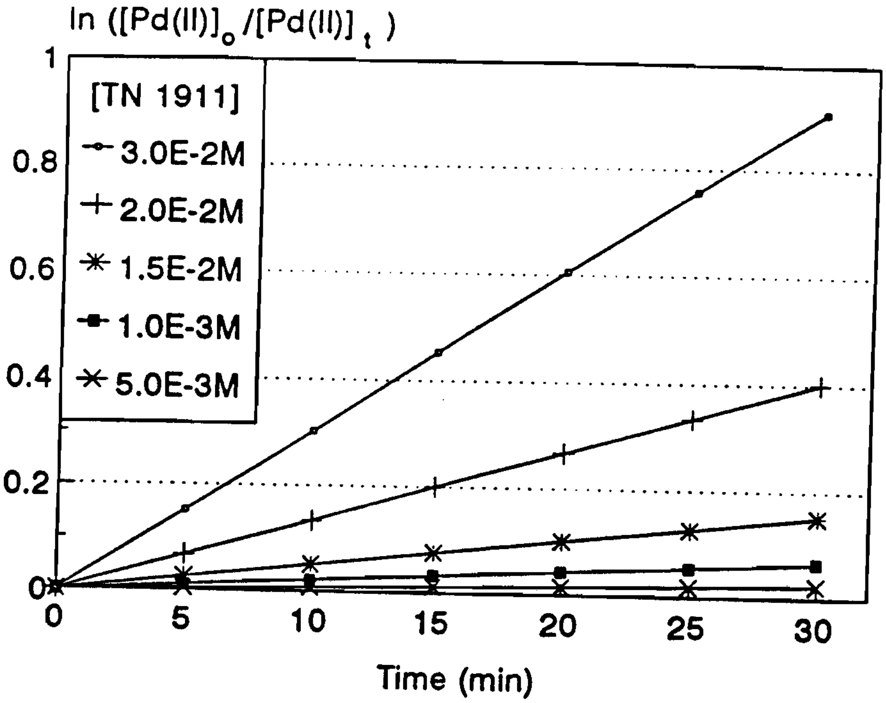


Figure 6.4 First order plots of Pd(II) extraction data at various TN 1911 concentrations.

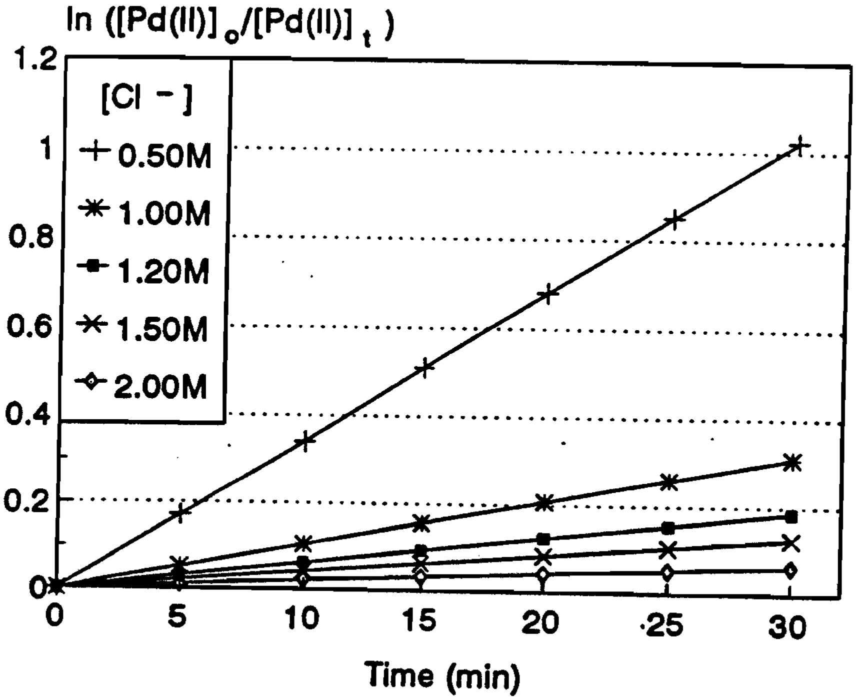


Figure 6.5 First order plots of Pd(II) extraction data at various Cl^- concentrations.

Table 6.1 Kinetic analysis of the TN 2336 Pd(II) extraction data at 25°C

A) The dependency on $[H^+]$

$[PdCl_4^{2-}]_{feed}=1.0\times10^{-3}M$, $[Cl\text{-}]_{feed}=2.00M$ (HCl+NaCl) $[TN\ 2336]_{org}=2.0\times10^{-2}M$

$[H^+]$ (mol/L)	$\ln[H^+]$	k_{obs} (s^{-1})	$\ln k_{obs}$
0.20	-1.609	5.79×10^{-5}	-9.726
0.50	-0.693	6.20×10^{-5}	-9.688
1.00	0.000	6.58×10^{-5}	-9.629
1.50	0.406	6.73×10^{-5}	-9.606
2.00	0.693	6.76×10^{-5}	-9.602

slope of $\ln k_{obs}$ vs $\ln[H^+]=0.070\pm0.005$

B) The dependency on [TN 2336]

$[PdCl_4^{2-}]_{feed}=1.0\times10^{-3}M$, $[HCl]_{feed}=2.00M$

[TN 2336] (mol/L)	ln [TN 2336]	k_{obs} (s^{-1})	$\ln k_{obs}$
5.0×10^{-3}	-5.298	4.46×10^{-6}	-12.320
1.0×10^{-2}	-4.605	1.24×10^{-5}	-11.298
1.5×10^{-2}	-4.199	2.45×10^{-5}	-10.580
2.0×10^{-2}	-3.912	5.36×10^{-5}	-9.834
3.0×10^{-2}	-3.507	1.65×10^{-4}	-8.709

slope of $\ln k_{obs}$ vs $\ln[TN\ 2336]_{org}=1.98\pm0.06$

C) The dependency on $[Cl^-]$

$[PdCl_4^{2-}]_{feed}=1.0\times10^{-3}M$, $[H^+]_{feed}=2.00M$ ($HCl+H_2SO_4$) $[TN\ 2336]_{org}$ $=2.0\times10^{-2}M$

$[Cl^-]$ (mol/L)	ln $[Cl^-]$	k_{obs} (s^{-1})	ln k_{obs}
0.20	-1.609	3.68×10^{-3}	-5.605
0.50	-0.693	7.63×10^{-4}	-7.178
1.00	0.000	2.52×10^{-4}	-8.286
1.20	0.182	1.36×10^{-4}	-8.903
1.50	0.406	8.41×10^{-5}	-9.384
2.00	0.693	5.30×10^{-5}	-9.845

slope of ln k_{obs} vs ln $[Cl^-]$ = -1.9±0.1

Plots of ln (k_{obs}) as a function of ln (of each parameter) helped to determine the individual orders. These plots are presented in Figures 6.6 to 6.8 for TN 1911 and in Table 6.1 for TN 2336. According to these data the extraction rate is zero order (0.12±0.01) in terms of $[H^+]$, second order (2.0±0.2) in terms of $[HQ]_{org}$ and -2 (-1.97±0.05) in terms of $[Cl^-]$ for TN 1911. The respective values for TN 2336 are: 0 (0.070±0.005), 2 (1.98±0.06) and -2 (-1.9±0.1). It is noteworthy that all the experimentally determined partial orders of the reaction are integers. On the basis of the above data, the apparent rate expression for the extraction of Pd(II) by both TN 1911 and TN 2336 is described by the following rate law:

$$-d[PdCl_4^{2-}]/dt = k_{ext}\,[PdCl_4^{2-}]\,[HQ]^2_{org}\,[Cl^-]^{-2} \qquad (6.3)$$

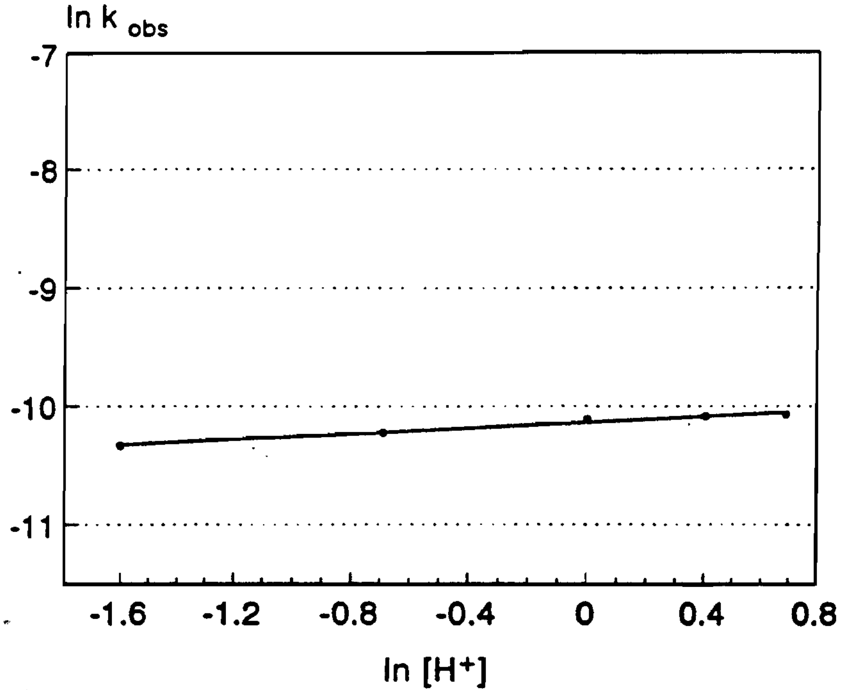


Figure 6.6 Log-log plot of the observed extraction rate constant, ln k_{obs}, versus ln $[H^+]$.

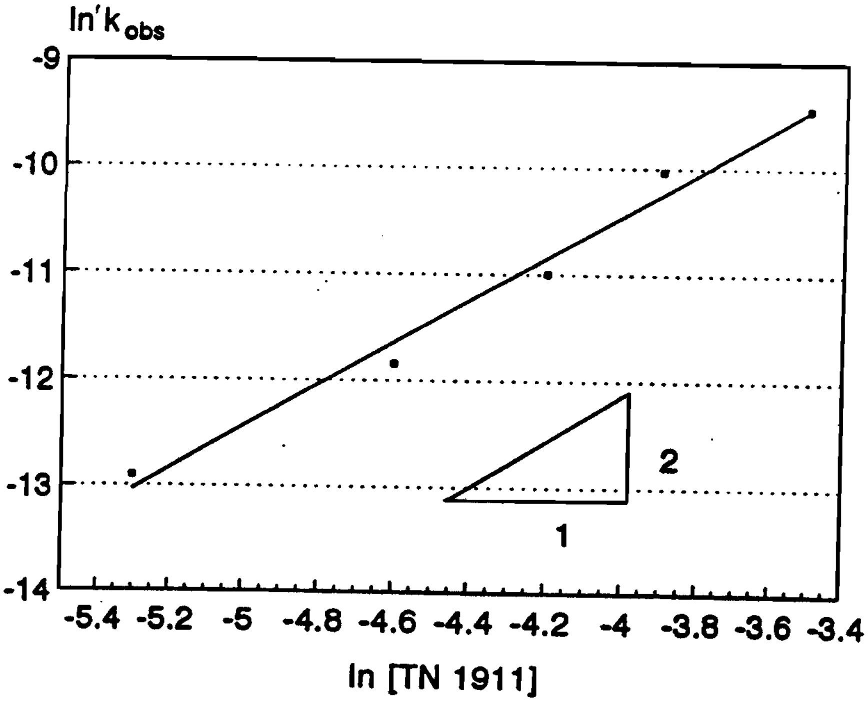


Figure 6.7 Log-log plot of the observed extraction rate constant, ln k_{obs}, versus ln [TN 1911] in $CHCl_3$.

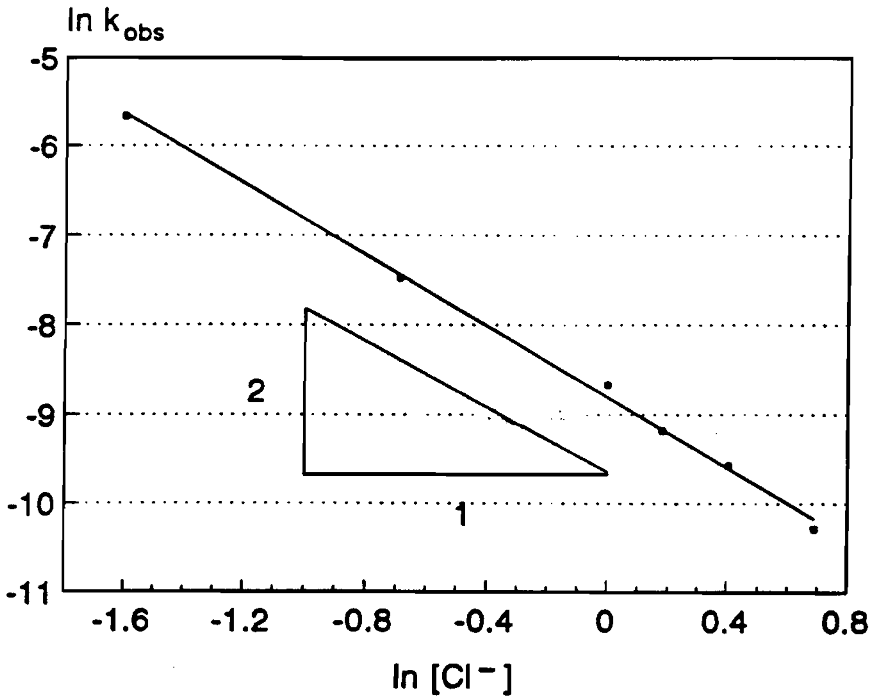


Figure 6.8 Log-log plot of the observed extraction rate constant of Pd(II), ln k_{obs}, versus ln [Cl⁻].

The second-order dependency with respect to the extractant concentration has also been observed by Ma and Freiser (8) who studied the extraction of Pd(II) with Kelex 100, another 7-substituted 8-hydroxyquinoline derivative similar to TN 1911 and TN 2336 investigated in the present work (5) [Chapter 4].

6.4.4 Extraction Mechanism

The following reaction mechanism has been reported by Ma and Freiser (8) to interpret the extraction kinetics of Pd(II) from chloride solutions with Kelex 100.

$HQ_{org} \rightleftarrows HQ$	fast	(6.4)
$HQ + H^+ \rightleftarrows H_2Q^+$	fast	(6.5)
$PdCl_4^{2-} + H_2Q^+ \rightleftarrows PdCl_2Q^- + 2H^+ + 2Cl^-$	fast	(6.6)

$$PdCl_2Q^- + H_2Q^+ \rightleftarrows PdQ_2 + 2H^+ + 2Cl^- \qquad \text{r.d.s.} \qquad (6.7)$$

$$PdQ_2 \rightleftarrows PdQ_{2org} \qquad \text{fast} \qquad (6.8)$$

In the above scheme reaction the subscript "org" indicates species in the organic phase and r.d.s. indicates the rate-determining step. In other words these investigators postulated the addition of the second ligand molecule to be the rate limiting step. However, the same authors did not explicitly define the site of the rate limiting step, but it seems very likely from their paper that they consider it to occur at the interface. Despite, the reaction orders and the overall rate equilibrium developed in this work agree with that of Ma and Freiser (8), nevertheless, the present authors interpret the results in terms of a homogeneous (within the organic phase) rate limiting step. This is done because of the apparent lack of dependency of the reaction rate on interfacial area (within the range of mixing conditions tested). Thus, in a radical departure from the previous conventional line of thought the present authors propose the following mechanism (only the major steps are indicated).

Step 1: Protonation of the extractant

$$HQ_{org} + H^+ \overset{K_p}{\rightleftarrows} H_2Q^+_{org} \qquad \text{fast} \qquad (6.9)$$

Step 2: Formation and interfacial transfer of the ion-pair

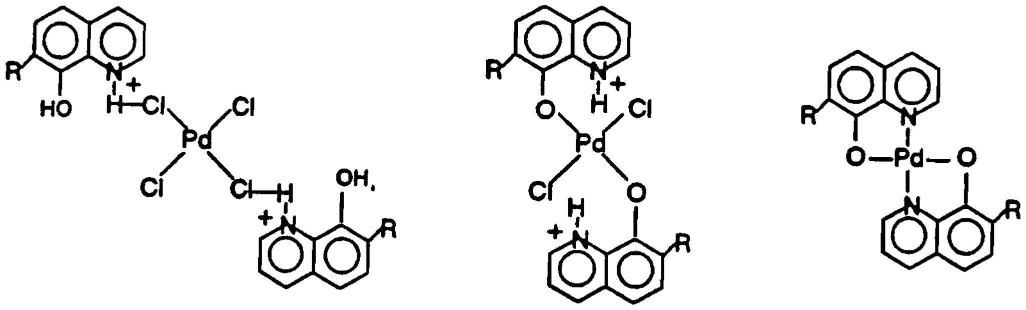
$$PdCl_4^{2-} + 2H_2Q^+_{org} \overset{K_{ip}}{\rightleftarrows} \underset{(I)}{[PdCl_4^{2-}\cdot(H_2Q^+)_2]_{org}} \qquad \text{fast} \qquad (6.10)$$

Step 3: Intramolecular transformation of the ion-pair to the chelate

$$[PdCl_4^{2-}\cdot(H_2Q^+)_2]_{org} \rightarrow \underset{(II)}{[Pd(HQ)_2Cl_2]_{org}} + 2H^+ + 2Cl^- \quad \text{r.d.s} \qquad (6.11)$$

$$[Pd(HQ)_2Cl_2]_{org} \rightleftarrows \underset{(III)}{PdQ_{2org}} + 2H^+ + 2Cl^- \qquad \text{fast} \qquad (6.12)$$

The structures of complexes I to III are illustrated in Figure 6.9. According to the proposed mechanism very fast interfacial transfer of Pd(II) in the organic phase as an ion-pair occurs first and this is followed by slow rearrangement of the ion-pair into a chelate.



(I) (II) (III)

Figure 6.9 The structures of complexes $[PdCl_4^{2-}\cdot(H_2Q^+)_2]$ (I), $[[Pd(HQ)_2Cl_2]$ (II) and $[PdQ_2]$(III).

This homogeneous reaction mechanism is in accordance with the observation that agitation speed and interfacial area had no effect on the extraction kinetics. Also, the postulated rate limiting step is in agreement with the experimentally determined reaction orders. Here is how the reaction order may be explained. The forward rate of the rate determining step (reaction 6.11) should be:

$$r_f = k_f\,[PdCl_4^{2-}\cdot(H_2Q^+)_2]_{org}\,[H^+]^{-2}\,[Cl^-]^{-2} \qquad (6.13)$$

but from step 2,

$$K_{ip} = [PdCl_4^{2-}\cdot(H_2Q^+)_2]_{org}/[PdCl_4^{2-}][H_2Q^+]^2_{org} \qquad (6.14)$$

and from step 1,

$$K_p = [H_2Q^+]_{org}/[HQ]_{org}[H^+] \tag{6.15}$$

Substituting $[PdCl_4^{2-} \cdot (H_2Q^+)_2]_{org}$ and $[H_2Q^+]_{org}$ from equations 6.14 and 6.15 respectively into equation 6.13 one gets:

$$r_f = k_f K_p K_{ip} \, [PdCl_4^{2-}] \, [HQ]^2_{org} [Cl^-]^{-2} \tag{6.16}$$

or $$r_{ext} = k_{ext} \, [PdCl_4^{2-}] \, [HQ]^2_{org} \, [Cl^-]^{-2} \tag{6.17}$$

where $k_{ext} = k_f K_p K_{ip}$.

Thus there is full agreement between the observed reaction orders and the postulated reaction mechanism. The values of k_{ext} were calculated from Eq. 6.18.

$$\ln k_{ext} = \ln k_{obs} - 2\ln [HQ]_{org} + 2\ln [Cl-] \tag{6.18}$$

The values of k_{ext} for TN 1911, TN 2336 and Kelex 100 are given in Table 6.2. On the same Table the k_{ext} for Kelex 100 is listed. This value was calculated by the present authors using the k_{obs} data reported by Ma and Freiser (8). It can be seen the value of k_{ext} for TN 1911 to be equal to that of Kelex 100. From a steric point of view the two derivatives are equivalent, i.e. they both have a branch at the α-position of the R group which hinders the complex formation reaction via the strengthening of the intramolecular hydrogen bonding (6) [Chapter 4]. On the other hand TN 2336, which is sterically-free, exhibits higher k_{ext}. Similar with k_{ext}, the k_{strip} values were determined from the k_{obs} data of the stripping reactions. The k_{strip} values are given in Table 6.2. Once more TN 2336 outperforms TN 1911.

Table 6.2 Extraction and stripping rate constants for Pd(II) with 7-substituted 8-HQ derivatives at 25 °C

Extractant	k_{ext} (s^{-1})	k_{strip} ($\times 10^{-6}$ s^{-1})	Ref
TN 1911	0.36±0.05	6.8±0.3	This work
TN 2336	0.6±0.1	8.9±0.3	This work
Kelex 100	0.40±0.09	N/A*	8

* Not available.

6.4.5 Stripping Kinetics

In a similar way as above, the stripping rate equations were derived. First order plots depicting the effects of $[H^+]$ (0.20M-1.50M), $[Cl^-]$ (0.20M-1.50M) and on stripping kinetics are presented in Figures 6.10 and 6.11 for TN 1911 and in Table 6.3 for TN 2336 respectively. The linearity of the plots suggests first order dependency in terms of $[PdQ_2]_{org}$. Plots of ln k_{obs} as a function of ln $[H^+]$ (Figure 6.12) and ln $[Cl^-]$ (Figure 6.13) revealed the following orders for TN 1911 (2.06±0.04 and 2.1±0.1). The corresponding results for TN 2336 (2.03±0.06 and 2.08±0.09) are summarized in Table 6.3. On the basis of the above data, the rate expression for the stripping of Pd(II) for both TN 1911 and TN 2336 is described by the following rate law:

$$d[PdCl_4^{2-}]/dt = k_{strip}\,[PdQ_2][H^+]^2\,[Cl^-]^2 \qquad (6.19)$$

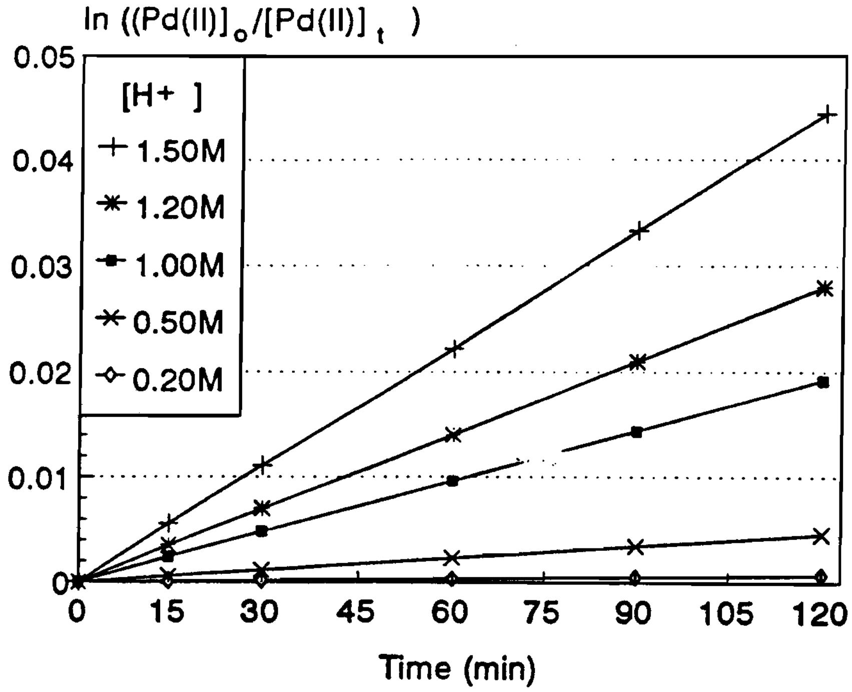


Figure 6.10 First order plots of Pd(II) stripping data at various H^+ concentrations.

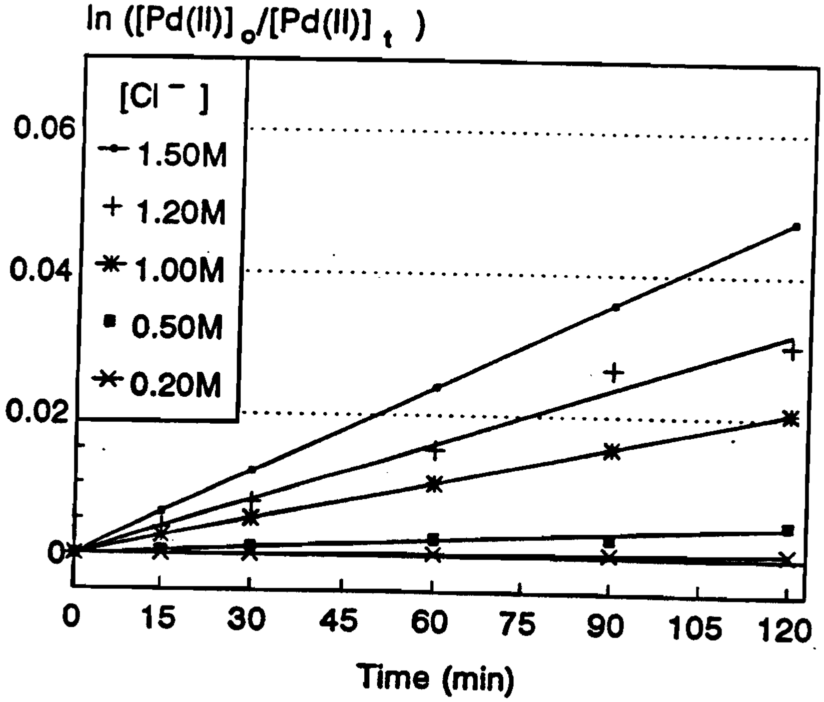


Figure 6.11 First order plots of Pd(II) stripping data at various Cl^- concentrations.

Table 6.3 Kinetic analysis of the TN 2336 Pd(II) stripping data at 25 °C

A) The dependency on $[H^+]$

$[PdQ_2]_{org} = 1.0 \times 10^{-2} M$, $[Cl^-]_{feed} = 1.50 M$ (HCl+NaCl)

$[H^+]$ (mol/L)	ln $[H^+]$	k_{obs} (s^{-1})	ln k_{obs}
0.20	-1.609	1.15×10^{-7}	-15.978
0.50	-0.693	7.43×10^{-7}	-14.113
1.00	0.000	3.04×10^{-6}	-12.704
1.20	0.182	4.41×10^{-6}	-12.332
1.50	0.406	6.93×10^{-6}	-11.879

slope of ln k_{obs} vs ln $[H^+]$ = 2.03±0.06

b) The dependency on $[Cl^-]$

$[PdQ_2]_{org} = 1.0 \times 10^{-2} M$, $[H^+]_{feed} = 1.50 M$ ($HCl + H_2SO_4$)

$[Cl^-]$ (mol/L)	ln $[Cl^-]$	k_{obs} (s^{-1})	ln k_{obs}
0.20	-1.609	1.31×10^{-7}	-15.848
0.50	-0.693	8.89×10^{-7}	-13.933
1.00	0.000	3.78×10^{-6}	-12.486
1.20	0.182	5.52×10^{-6}	-12.107
1.50	0.406	8.83×10^{-6}	-11.637

slope of ln k_{obs} vs ln $[Cl^-]$ = 2.08±0.09

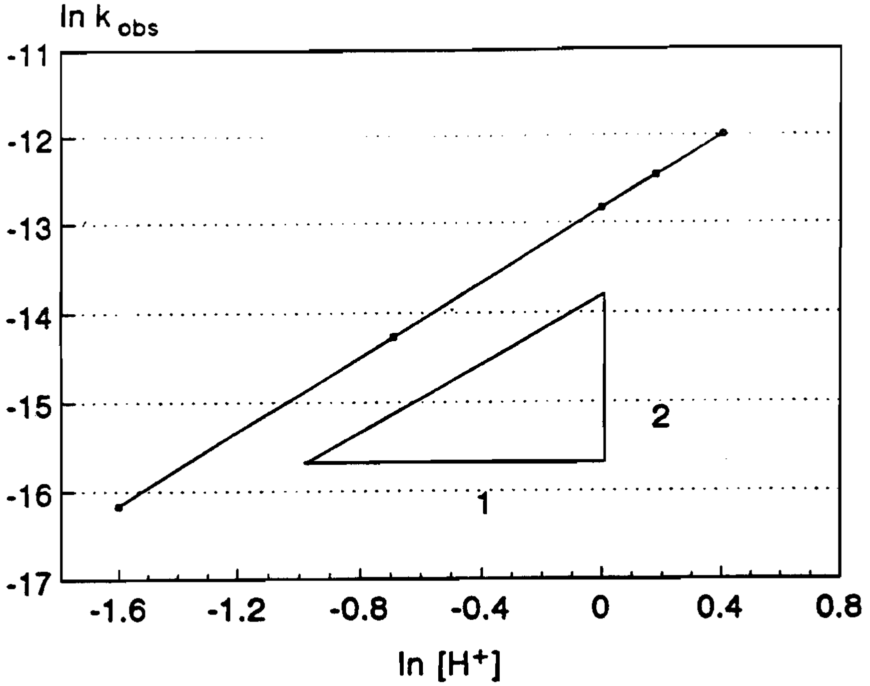


Figure 6.12 Log-log plot of the observed stripping rate constant, ln k_{obs}, versus ln $[H^+]$.

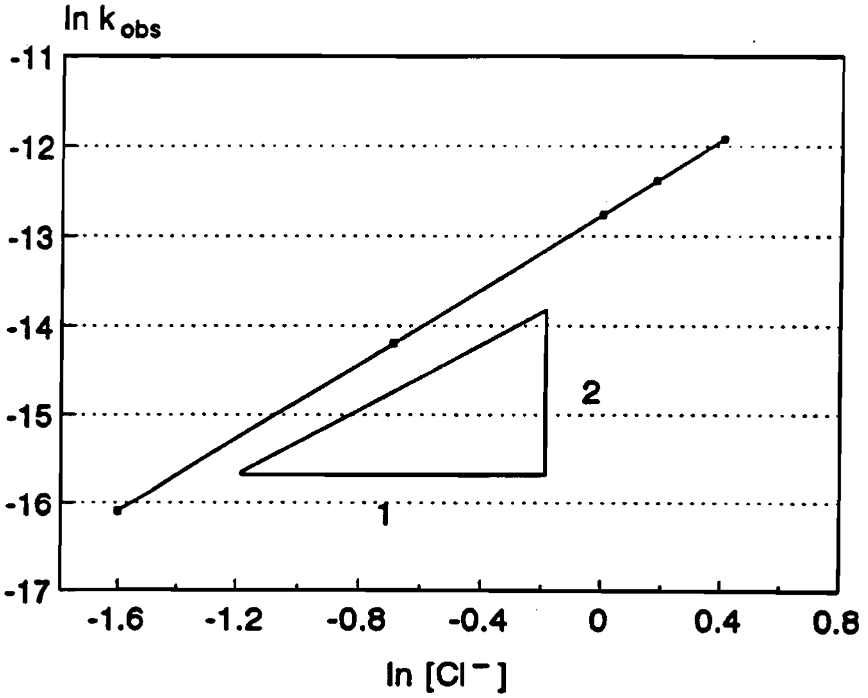


Figure 6.13 Log-log plot of the observed stripping rate constant, ln k_{obs}, versus ln $[Cl^-]$.

6.4.6 Overall Rate

Now that the individual rates have been determined the overall or net rate ,r_{net}, of the reversible solvent extraction reaction (Eq. 6.1) can be defined as:

$$r_{net} = r_{ext} - r_{strip} \tag{6.20}$$

or

$$r_{net} = -d[PdCl_4^{2-}]/dt = k_{ext}\,[PdCl_4^{2-}]\,[HQ]^2_{org}\,[Cl^-]^{-2} \\ -k_{strip}\,[PdQ_2]_{org}\,[H^+]^2\,[Cl^-]^2 \tag{6.21}$$

At equilibrium $r_{net} = 0$

or

$$k_{ext}/k_{strip} = [PdQ_2]_{org}\,[H^+]^2\,[Cl^-]^4/[PdCl_4^{2-}]\,[HQ]^2_{org} \tag{6.22}$$

6.4.7 Extraction of Pd(II) in the Presence of Pt(IV)

Substituted 8-hydroxyquinoline derivatives like the ones studied in this work, have been proposed for the co-extraction of Pt(IV)/ Pd(II) and the separation of the above metals by differential stripping (4). It was of interest therefore to consider how the equilibria of Pd(II) reported in (6) [Chapter 4] and its kinetics are affected by the presence of Pt(IV).

6.4.8 Binary Metal Distribution

The distribution of Pt(IV) and Pd(II) in mixed metal solutions was briefly studied. Figure 6.14 shows the concentration of both metals in the organic phase as a function of the number of consecutive loading steps (cross-current contacting). According to this Figure, as the number of contacting steps with fresh portions of feed solution increases, the Pd(II) concentration in the organic phase increases as well.

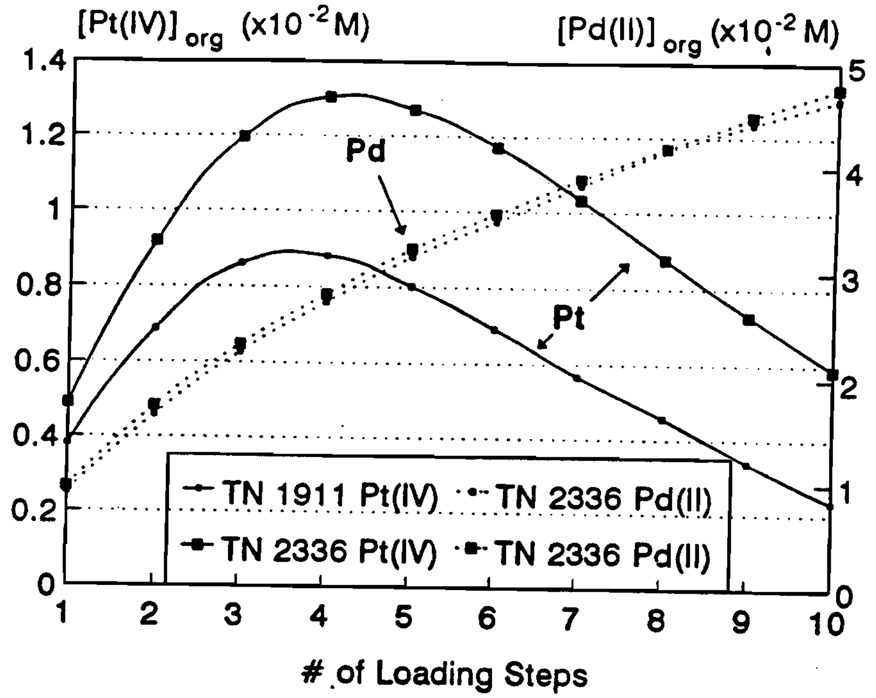


Figure 6.14 Pt(IV) and Pd(II) co-extraction from mixed metals solution as a function of number of loading stages.

However, the Pt(IV) concentration starts to decrease gradually. The following reaction scheme is suggested to explain this exchange process. According to this scheme Pt(IV) is extracted ahead of Pd(II) as $PtCl_6^{2-}\cdot(H_2Q^+)_2$ (Reaction 6.23). However, due to the thermodynamic predominance of the PdQ_2 chelate formation reaction (Reaction 6.24) Pt(IV) is gradually crowded out of the organic phase (Reaction 6.25).

<u>Step 1</u> Metal Co-extraction

$PtCl_6^{2-} + 2[H_2Q^+Cl^-]_{org} \rightleftarrows [PtCl_6^{2-}\cdot(H_2Q^+)_2]_{org} + 2Cl^-$ fast (6.23)

$PdCl_4^{2-} + 2[HQ]_{org} \rightleftarrows [PdQ_2]_{org} + 2H^+ + 4Cl^-$ slow (6.24)

Step 2 Metal Exchange Reaction

$$[PtCl_6^{2-}\cdot(H_2Q^+)_2]_{org} + PdCl_4^{2-} \rightleftarrows [PdQ_2]_{org} + PtCl_6^{2-} + 4H^+ + 4Cl^- \qquad (6.25)$$

The above scheme is in agreement with the equilibrium constant reported earlier for reaction 6.22 (log K_{ex}=3.48 and 3.62) for TN 1911 and TN 2336 (7) [Chapter 5] and for reaction 6.23 (log K_{ex}= 5.59 and 5.84) for TN 1911 and TN 2336 (6) [Chapter 4] respectively. Extraction via ion-pair formation is thought to be very fast (and this has been observed in our laboratory) (7), since the nature of this process is largely electrostatic. However, the formation of the chelate complex is slow as chemical bonds have to develop between the bonding sites of the organic reagent and the metal ion. Because of the observed competition between Pt(IV) and Pd(II) during co-extraction of the two metals, caution should be exercised in selecting the suitable mixing time. Thus for feeds having high Pt(IV)/Pd(II) ratio, short mixing times (about 3 to 5 minutes) should be used in order to favour the extraction of the most abundant metal, Pt(IV). However, for feeds having high Pd(II)/Pt(IV) ratio longer mixing times (about 10 to 15 minutes) should be used instead to favour the extraction of the most abundant metal, Pd(II), (9).

6.4.9 Kinetics of Pd(II) Extraction with Pt(IV) Loaded 8-HQ Reagents

The kinetics of reaction 6.25 were measured under the same experimental conditions used to study the extraction kinetics of Pd(II) with the unloaded extractant, i.e. reaction 6.1. The only difference was that the extractant was previously saturated with Pt(IV) prior to the extraction of Pd(II). The kinetic results are presented in Table 6.4.

Table 6.4 Observed extraction rate constants of Pd(II) with Pt(IV)-loaded TN 1911 and TN 2336 at 25 °C

A) The dependency on $[H^+]$

$[PtCl_6^{2-}(H_2Q^+)_2]_{org} = 1.0 \times 10^{-2}$M, $[Cl^-]_{feed} = 2.00$M (HCl+NaCl)

$[H^+]$ (mol/L)	k_{obs} (s^{-1})	
	TN 1911	TN 2336
0.20	2.43×10^{-5}	4.28×10^{-5}
0.50	2.49×10^{-5}	4.71×10^{-5}
1.00	3.00×10^{-5}	4.87×10^{-5}
1.50	3.04×10^{-5}	5.05×10^{-5}
2.00	3.10×10^{-5}	5.21×10^{-5}

slope of ln k_{obs} vs ln $[H^+]$ = 0.12 ± 0.02 (TN 1911) and 0.081 ± 0.006 (TN 2336)

B) The dependency on $[PtCl_6^{2-}(H_2Q^+)_2]_{org}$

$[HCl]_{feed} = 2.00$M

$[PtCl_6^{2-}(H_2Q^+)_2]_{org}$ (mol/L)	k_{obs} (s^{-1})	
	TN 1911	TN 2336
5.00×10^{-3}	9.80×10^{-6}	1.67×10^{-5}
1.00×10^{-2}	2.72×10^{-5}	4.67×10^{-5}
1.50×10^{-2}	6.16×10^{-5}	9.27×10^{-5}
2.00×10^{-2}	1.65×10^{-4}	2.06×10^{-4}
3.00×10^{-2}	3.84×10^{-4}	5.93×10^{-4}

slope of ln k_{obs} vs ln $[PtCl_6^{2-}(H_2Q^+)_2]_{org}$ = 2.0 ± 0.2 (TN 1911) and 2.1 ± 0.2 TN 2336)

C) The dependency on [Cl$^-$]

$[PdQ_2]_{org} = 1.0 \times 10^{-2}$M, $[H^+]_{feed} = 2.00$M ($HCl + H_2SO_4$)

[Cl$^-$] (mol/L)	k_{obs} (s^{-1})	
	TN 1911	TN 2336
0.20	2.61×10^{-3}	2.72×10^{-3}
0.50	4.26×10^{-4}	5.80×10^{-4}
1.00	1.29×10^{-4}	1.84×10^{-4}
1.20	7.73×10^{-5}	1.00×10^{-4}
1.50	5.21×10^{-5}	6.18×10^{-5}
2.00	2.57×10^{-5}	3.29×10^{-5}

slope of ln k_{obs} vs ln [Cl$^-$]= -1.9±0.1 (TN 1911) and
-2.0±0.1 (TN 2336)

Again, for this series of tests new extraction rate constants, k_{ext}, were calculated as described earlier. The calculated values of k_{ext} for TN 1911 and TN 2336 are 0.29±0.04 s^{-1} and 0.43±0.09 s^{-1} respectively. Comparison of these k_{ext} with those for the unloaded extractant (Table 6.2) reveals that the presence of Pt(IV) in the organic phase has a weak detrimental effect on the kinetics of Pd(II) extraction.

6.5 Summary

The extraction and stripping kinetics of Pd(II) from chloride media with 7-substituted 8-hydroxyquinolines were studied. The two 8-HQ derivatives tested were TN 1911, an unsaturated and sterically-hindered C_{11}-C_{13} alkenyl derivative and TN 2336, a saturated and sterically-free C_{11}-C_{13} alkyl derivative. The reaction orders were determined to be: 1 ([$PdCl_4^{2-}$]), 0 ([H^+]), 2 ($[HQ]_{org}$) and -2 ([Cl$^-$] for the extraction reaction and 1 ($[PdQ_2]_{org}$), 2 ($[H^+]$) and 2 ($[Cl^-]$) for the stripping reaction with both extractants. The respective rate constants for TN 1911 and TN 2336 were determined to be ($0.36\ s^{-1}$ and $0.6\ s^{-1}$) for the extraction and for stripping ($6.8 \times 10^{-6}\ s^{-1}$ and $8.9 \times 10^{-6}\ s^{-1}$). TN 2336, the sterically-free extractant, was found to exhibit faster kinetics in comparison to TN 1911 due to its weaker intramolecular hydrogen bonding (2). The observed kinetic behaviour has been interpreted in terms of a mechanism which involves the fast formation and interfacial transfer of the ion-pair $PdCl_4^{2-} \cdot (H_2Q^+)^2$ (where H_2Q^+ represents the protonated extractant) and the subsequent slow intramolecular transformation of the ion-pair to a chelate complex within the organic phase.

In the presence of Pt(IV), Pd(II) is extracted at a somewhat slower kinetics. Co-extraction of the two metals proceeds via the fast loading of Pt(IV) as $PtCl_6^{2-} \cdot (H_2Q^+)_2$ and the parallel slow loading of Pd(II) as PdQ_2. Under conditions of competition, i.e. near the saturation of the organic phase an exchange between the two metals occurs which leads to the crowding out of Pt(IV) and the dominant loading of Pd(II). Both thermodynamic and kinetic factors point out to this loading behaviour.

6.6 Acknowledgements

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Chapter 7

Synopsis

7.1 Conclusions

Already, at the end of each chapter the specific conclusions, findings deduced from each part of the work have been outlined. Here, only the major global conclusions of the overall research are given.

1. Extensive GC-MS characterization revealed TN 1911 to be a mixture of mono-unsaturated isomers resembling Lix 26 but having a higher purity. The isomers were found, with the aid of proton-NMR, to be of two types, (a) structural isomers. i.e. branched and normal side chains, and (b) position isomers, i.e. having olefinic protons located along the side chain at different positions. In terms of purity, the various 7-substituted 8-HQ derivatives were found to be 93% (TN 1911), 81% (TN 2181), 80% (TN 2336), 64% (TN 2221), 63% (Lix 26), 78% (Kelex 100) and 88% (Kelex 100S).

2. It has been demonstrated that the extraction power of the 7-substituted 8-HQ derivatives *vis-à-vis* Pd(II) and Pt(IV) is directly related to the extent and strength of intramolecular hydrogen bonding occurring between the phenolic proton and the nitrogen heteroatom of the 8-HQ substrate. Depending on the length and orientation of the substituent group in the 7-position, the derivatives were classified having either weak (TN 2336 and TN 2181) or strong (TN 1911 and TN 2221) intramolecular hydrogen bonding. The reagents with weak intramolecular hydrogen bonding exhibited low steric hindrance. When it comes to metal extraction, steric effects were found to

overweigh in significance electronic effects arising from the presence or not of an unsaturation near the α-position of the substituent group.

3. The degree of acid (HCl) and water extracted by 7-substituted 8-HQ derivatives was measured and the equilibrium constant of the protonation reaction was determined to be 0.49 ± 0.02, 0.55 ± 0.02 and 0.32 ± 0.03 for TN 1911, TN 2336 and Kelex 100 respectively. Thus, the relative order of basicity of the nitrogen atom present in those extractants is as follows:

   TN 2336 > TN 1911 > Kelex 100

   At 2.0M HCl and higher, all extractant becomes fully protonated.

4. The stoichiometry of the palladium extraction reaction was deduced to be:

   $$PdCl_4^{2-} + 2HQ_{org} \rightleftarrows PdQ_{2org} + 2H^+ + 4Cl^-$$

   The log of extraction equilibrium constants, log K_{ex}, were found to be 5.59 ± 0.05 and 5.84 ± 0.05 for TN 1911 and TN 2336 respectively. The superior performance of TN 2336 has been linked to its low steric hindrance. In terms of stripping, mixed HCl/$MgCl_2$ media were found to be more effective than single HCl solutions.

5. The stoichiometry of the extraction of Pt(IV) with 8-HQ derivatives was determined to be:

   $$PtCl_6^{2-} + 2H_2Q^+Cl^-_{org} \rightleftarrows PtCl_6^{2-}\cdot(H_2Q^+)_{2org} + 2Cl^-$$

The log extraction equilibrium constants were found to be: 3.48±0.06 and 3.62±0.06 for TN 1911 and TN 2336 respectively. The formation of the ion-pair $PtCl_6^{2-} \cdot (H_2Q^+)_2$ was validated with indirect UV-Visible and infrared spectroscopic analysis.

The stripping of platinum was found to be favoured by temperature and pH elevation. The ease of stripping is the inverse to that of extraction, i.e. TN 1911 strips better than TN 2336.

6. In terms of kinetics, Pt(IV) is extracted in a matter of a few minutes -typical for an ion-pair formation reaction- but, Pd(II) extraction kinetics are relatively slow. The rate law of PdQ_2 extraction-stripping was determined to be the following:

$$r_{net} = k_{ext} [PdCl_4^{2-}] [HQ]^2_{org} [Cl^-]^{-2} - k_{strip} [PdQ_2]_{org} [H^+]^2 [Cl^-]^2$$

k_{ext} and k_{strip}, were found to be 0.36±0.05 and 6.8±0.3 $(\times 10^{-6})$ for TN 1911 and 0.6±0.1 s^{-1} and 8.9±0.3 $(\times 10^{-6})$ s^{-1} for TN 2336 respectively.

7. The extraction reaction was found to be independent of the interfacial area and the agitation speed within the agitation range studied (350-1300 rpm). This prompted the advancement of a novel extraction mechanism according to which Pd(II) extraction proceeds through the fast formation and interphase transfer of the ion-pair and the slow intramolecular transformation of the latter to a chelate complex within the organic phase.

8. When both metals, i.e. Pt(IV) and Pd(II) are present in the aqueous phase co-extraction occurs provided that excess of extractant is used. However,

under conditions of competition, i.e. near saturation of the organic phase an exchange between the two metals takes place which leads to the crowding out of Pt(IV) and the dominant loading of Pd(II). Both thermodynamic and kinetic factors point out to this loading scheme.

7.2 Claims to Originality

Several aspects of the present work constitute according to the opinion of the author original contributions to knowledge. The most important of them are outlined below.

1. The quantification of the presence of isomers in TN 1911 and Lix 26 is reported for the first time. Other characterization features of 7-substituted 8-HQ derivatives are considered novel as well.

2. The stoichiometry of the hydrochloric acid extraction reaction and the determination of the equilibrium constants of the respective protonation reactions for TN 1911, TN 2336 and Kelex 100 are reported for the first time. The concomitant extraction of water along with HCl and the relation ship between the two are also thought to be novel.

3. The use of intramolecular hydrogen bonding phenomena to rationalize the extraction and stripping performance of 7-substituted 8-HQ derivatives for Pd(II) and Pt(IV) from chloride media is another original contribution to knowledge.

4. The determination of stoichiometries and equilibrium constants for the respective extraction of Pd(II) and Pt(IV) with these new 8-HQ derivatives

is also novel.

5. The ability of tridecanol to extract Pt(IV) under very acidic feed conditions is also reported for the first time.

6. The integrated extraction-stripping rate law for PdQ_2 and the two steps extraction mechanism, (i) fast interfacial transfer of $PdCl_4^{2-}$ as an ion-pair and , (ii) slow intramolecular transformation of the latter to PdQ_2 are new contributions as is the measurement of the kinetics of the exchange reaction between Pt(IV) and Pd(II).