EXTRACTION STUDIES ON SOME PLATINUM METALS USING ORGANOPHOSPHORUS EXTRACTANTS

Ph.D. THESIS

by

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CHAPTER I

INTRODUCTION

There is probably no material that has shaped the progression of mankind more than metals. Metals are as old as human civilization and their history can be traced back to 6000 BC. During the ancient times, locations rich in ores tended to make the people living in that area richer and more powerful. Metal is so important in the history of mankind because of its influence on industry. Today's fast growing technical world has witnessed many examples when a rare, lesser known and worthy metal has occupied important and indispensable position in many fields, once its particular use was realized. The later half of the twentieth century has witnessed the importance of metals in several technical discoveries which have completely revolutionized the approach of human life. Few such metals belong to Platinum Group Metals (PGMs).

Platinum group metals consist of six elements–platinum, palladium, rhodium, iridium, ruthenium and osmium. PGMs together with gold and silver form the family of precious metals. PGMs are generally used in applications which depend strongly on their unique properties, such as their excellent inertness with corrosion and oxidation, biocompatibility, high melting temperature, good conductivity and electronic and catalytic properties. The higher premium paid for PGMs is justified by their superior performance in specific applications. PGMs are most often used as catalysts because of their chemical stability, but are not limited to this role. Platinum metals have become vital in many technological fields such as automotive catalytic converters, catalysts in the chemical and petroleum refining and in jewellery making, electronics, glass industry and medical sciences. The growing areas are auto catalysts and jewellery. The PGMs are widely used as catalysts for a variety of chemical reactions such as hydrogenation, isomerisation, oxidation, dehalogenation, dehydrogenation and cyclization. These metals in pure form or alloyed with other metals are used in several high tech applications. Continuous research on the properties and qualities of platinum group metals is unearthing new applications every year.

These metals are extremely rare, owing in part to their low natural abundance and in part to the complex processes required for their extraction and refining. With the exception of small alluvial deposits of platinum, palladium, and iridosmine (an alloy of iridium and osmium), virtually no ore exists in which the major metal is from the platinum group. Platinum metals are usually highly disseminated in sulfide ores, particularly the nickel and copper. The most common ores of PGMs include laurite (RuS_2), irarsite [(Ir,Ru,Rh,Pt)AsS], osmiridium (Ir,Os), cooperite (PtS), and braggite [(Pt,Pd)S]. This makes the mutual separation of PGMs and their separation from associated metals a must to do task. The world's largest deposit is the Bushveld Complex of South Africa. Other major deposits include the Sudbury deposit of Ontario, Canada, and the Norilsk-Talnakh deposit of Siberia in Russia.

The availability of PGMs in used scrap materials contributes great economy of PGM usage and technological importance of these metals has created a never ending demand (1). The petroleum and petrochemical industries generate considerable amounts of spent catalysts with small but significant PGM content. The PGMs are the main active ingredients of these catalysts. Spent catalysts are classified by the North-American Environment protection Agency (EPA) as hazardous wastes because they may be pyrophoric, spontaneously combustible and release toxic gases. Although the amount of these metals in a commercial catalyst is very low, it corresponds to the main cost of this product (2, 3). When regeneration is no longer possible the so-called spent catalysts are usually treated in order to recover the noble metals present. Therefore, recycling of spent catalysts is an attractive way to lower the catalyst cost (4). This necessitates the development of indigenous methods for the recovery of PGMs from available sources.

Unlike other precious metals like gold and silver, which could be readily isolated in a comparatively pure state by simple fire refining, the platinum metals require complex aqueous chemical processing for their isolation and identification. Because these techniques were not available until the turn of the 19th century, the identification and isolation of the platinum group lagged behind silver and gold by thousands of years. As evident, the separation and purification of PGMs is difficult owing to their similar structures and chemical behaviours. Thus it is of paramount importance to develop efficient methods for the recovery and separation of platinum metals. This prompted the author to undertake studies on the extraction of various platinum group metals and their recovery from different matrices.

In the past few decades the hydrometallurgical processing of the metal ions has come up as a useful alternative to the commercial pyrometallugical operations. It may be important to point out here that for the use of PGMs in the catalysts and other hi-tech applications the purity of the metal is of paramount importance. The method should, therefore, be such that they can be easily recovered in high purity from their low concentrations present in secondary sources. One such technique which ideally suits to meet these requirements is liquid-liquid extraction. Liquid-liquid extraction is basically a phase distribution phenomenon in which a solute is distributed between two immiscible liquids as stated by Nernst's distribution law. Selectivity in liquid-liquid extraction is easy to attain because of the availability of a wide variety of extractants and diluents. The aqueous and organic phase parameters can be easily manipulated to attain a high separation factor.

During the second half of the twentieth century, the increased need for a variety of high purity products has resulted in the penetration of solvent extraction into practically every chemical process industry. The technique is fast, simple, versatile, environment friendly and involves relatively less operational cost. The transfer of extraction process from bench level to plant scale is easily accomplished in solvent extraction. Apart from facilitating pre-concentration, purification, separation and analysis of various materials it also elucidates some of the basics of chemistry. The extraction equilibria studies help in predicting the metal complex equilibria existing in the aqueous phase and also give an idea about the kinetic and thermodynamic aspects of the system. Though the process of extraction differs from metal to metal but three aspects are common to every metal extraction process. These are

(i) formation of an uncharged complex or extractable species,
(ii) distribution of extractable species, and
(iii) interaction of the extractable complex or species with the organic phase.

From time to time, a variety of extractants with different modes of extraction mechanism have emerged to provide effective separations. The classification of various extraction systems in a cohesive ordered form has been a difficult task to perform. Several attempts have been made to classify various extraction systems based on the mechanism of extraction and the nature of the extractant. However, one of the most convenient and acceptable classifications based on the mechanism of extraction and nature of the extractant was proposed by Marcus and Kertes (5) and also by De, Chalmers and Khopkar (6) as,

- (i) Distribution of simple molecules,
- (ii) Extraction by compound formation using chelating agents, acidic organophosphorus extractants, carboxylic and sulfonic acids,
- (iii) Extraction by solvation and
- (iv) Extraction by ion pair formation.

(A) DISTRIBUTION OF SIMPLE MOLECULES

This involves the distribution of simple covalent molecules, like I_2, $GeCl_4$, $HgBr_2$ and $AsBr_3$ between aqueous phase and inert organic solvents which do not contain atoms with pronounced donor properties.

(B) EXTRACTION BY COMPOUND FORMATION

The extractants falling under this category are frequently called as liquid cation exchangers. These reagents have a labile hydrogen ion which interchanges with the metal ion in aqueous phase, thus bringing about the required mass transfer. Despite, the similarity of the extraction reaction, there are some important differences between various reagents as regards their interaction with the metal ions. Taking into account these differences the extractants can be classified under three heads.

(i) Chelating Agents

The organic chelating agents act as weak acids, invariably neutralise the charge on the metal ion and satisfy the coordination number requirements. If the coordination sites remain vacant they may be occupied by the solvating molecules which sometimes may be the ligand itself. The well known extractants in this category are β-diketones, dithizone, 8-hydroxyquinoline, mono- and dioximes, nitrosophenols, nitrosoaryl hydroxylamines, hydroxamic acids and dithiocarbamates. Some of the acidic chelating agents commercially available in the market are LIX 63, LIX 64N, LIX 65N, LIX 70, SME 529, P5000 series (hydroxyoximes), Kelex 100 (oxine derivative) and Hostarex DKI6, LIX 54, X151 (β-diketones). Some examples of extracting species are $Th(C_9H_6ON)_4$, $Sr(C_9H_6ON)_2.2BuNH_2$ and $Sr(C_9H_6ON)_2.2C_9H_7ON$.

(ii) Acidic Organophosphorus Extractants

Alkyl phosphoric, phosphonic and phosphinic acids fall under this category. They extract metal ions by a cation exchange reaction between one or two acidic hydrogens of the extractant and the extractable metal ion. Formation of dimers and the solvation of metal-extractant complex by one or more extractant molecules are the two side reactions. The most commonly used extractants of this class are mono(2-ethylhexyl)phosphoric acid (H_2MEHP) and di(2-ethylhexyl)phosphoric acid (DEHPA). Besides these two, the other important commercial extractants are 2-ethylhexylphosphonic acid (PC-88A), dibutyl butylphosphonate (PC-44), bis(2,4,4-trimethylpentyl)phosphinic acid (Cyanex 272) and its sulphur analogues namely bis (2,4,4-trimethylpentyl)monothiophosphinic acid (Cyanex 302) and bis(2,4,4-trimethylpentyl)dithiophosphinic acid (Cyanex 301). Typical extracting species have the composition like UO_2X_2, CuX_2, $Be(X.HX)_2$ and $Fe(X.HX)_2$, where HX = di(2-ethylhexyl) phosphoric acid and X = phosphate ion.

(iii) Carboxylic and Sulphonic Acids

The solutions of carboxylic and sulphonic acids in non-polar organic liquids, being analogous to crosslinked resinous cation exchangers, frequently offer various advantages. They have the advantage of requiring only a pH adjustment of aqueous phase for clean separations. Different carboxy1ic, alkyl or aryl-alkyl sulphonic and sulphuric acids form salts with a number of metals including alkali and alkaline earths. The salts are generally soluble in aqueous solutions but exhibit an increased solubility in some organic liquids. The metal extraction is complicated by the aggregation of the acids. The most important commercial extractants of the carboxylic acid series are Naphthenic and Versatic acids. Some typical examples of the extracting species formed by this class of extractants are $(CoR_2.2RH_2)_2$, $(NiR_2.RH)_2$ and $ZnR_2.RH$.

(C) EXTRACTION BY SOLVATION

Some oxygenated solvents like ethers, esters, ketones and phosphorus esters solvate protons and neutral inorganic species making the extraction of the acids and salts feasible e.g. $HNO_3.TBP$, $H(TBP)_4.ReO_4$ and $Ce(NO_3)_4.(ether)_2$. One of the striking differences between the organophosphorus and oxygenated solvents is that water is completely eliminated from the organic phase in the former whereas it is necessarily a part of the complex in the latter. The phosphorus-bonded extractants have more or less completely phased out the ethers and ketones from the technological applications.

Tri-n-butylphosphate (TBP) is the most familiar extractant of this class. Trioctylphosphine oxide (TOPO) which shows highly increased extraction power is another important reagent of this class. The extraction power of these phosphorus based compounds increases significantly as the number of direct C-P linkages increases in the series phosphate-phosphonate-phosphinate-phosphine oxide. Cyanex 923 (mixture of four trialkylphosphine oxides), Cyanex 925 (mixture of two trialkylphosphine oxides) and Cyanex 471X (triisobutylphosphine sulphide) are also examples of this class of extractants. They help in the extraction of metal salts by solvation. The typical examples of extracting species are $UO_2(NO_3).2TOPO$, $ZrCl_4.2TOPO$ and $Th(NO_3)_4.2TOPO$.

(D) EXTRACTION BY ION PAIR FORMATION

This primarily involves the extraction of a species formed due to an interaction between an anionic metal species in the aqueous phase and the cation furnished by an organic base. The basic high molecular weight amines (HMWA) are able to extract the metals by forming the ion pairs with anionic metal complexes. The other extractable pairs formed by quaternary phosphonium, arsonium and phenylonium bases are also included under this category. Under this class of extractants high molecular weight amines (HMWA) have received maximum attention. These are popularly known as liquid anion exchangers. Some of the commercially available extractants of the category are primary amines-Primene-JMT, Primene 81R; secondary amines-Amberlite LA-1, Amberlite LA-2, Adogen 283; tertiary amines-Alamine 336, Adogen 364, Adogen 381, Adogen 382 and quaternary amines- Aliquat 336 and Adogen 464.

These are popularly known as liquid anion exchangers. Some of the typical extracting species are $R_3NH^+FeCl_4^-$, $(R_4N^+)_2ZnCl^{2-}_4$ and $(C_6H_5)_4As^+MnO_4^-$.

The application of solvent extraction into diverse fields can be gauged from the vastness of literature available on the subject. From time to time several researchers have reviewed the work carried out on different extraction systems (7, 8). The growth of literature on the subject is so enormous that subsequently the reviews started appearing on specific class of extractants (9-13) or the extractants for a group of metal ions (14-19). The proceedings of International Solvent Extraction Conference (ISEC) held periodically every three years provide valuable records of the developments and trends in solvent extraction To cite a few these were held at Kyoto (1990), New York (1993), Melbourne (1996), Barcelona (1999), Cape Town (2002), Beijing (2005), Tucson (2008) and Santiago (2011). The importance of the subject is reflected by the fact that the International Conferences on Analytical Chemistry and Separation Science and Technology devote a considerable time on solvent extraction of metal ions.

The studies on liquid-liquid extraction of metal ions have always enamoured professionals of different disciplines, namely chemists, hydrometallurgists, chemical engineers and environmentalists. The last few decades have seen a phenomenal rise in the application of this technique in hydrometallurgy. The widespread use of solvent extraction for metal recovery can be attributed to its economic feasibility and the built-in concentration step thereby providing an effective method for the beneficiation of low grade sources of metals. No doubt there is a voluminous literature on the extractants but the search for better systems with special objectives still continues. The present thesis is an endeavour in this direction.

A perusal of literature reveals that the commercial extractants of all the important categories namely chelating agents (20-23), carboxylic acids (24, 25), high molecular weight amines (26-29) and organophosphorus extractants (30-33) have been used for the extraction and separation of various metal ions. One feels a little diffident to comment on the relative merits and demerits of these extractants as far as their practical utility for the recovery of metals from leaner sources is concerned. From literature review it emerges out that not many of them have been used for the recovery of PGMs from different metal containing matrices. An idea about the utility of various extractants for the extraction and separation of PGMs can be had from the work carried out in last two decades cited in the proceeding text.

Among the chelating extractants Kelex 100 has been explored by various workers for the separation of PGMs. Antico and associates (20) proposed the extraction of Pd(II) with toluene solution of Kelex 100 from chloride medium in the presence of SCN^- (thiocyanide). The results revealed that SCN^- behaves as a catalytic reagent. Alam and Inoue (21) investigated the extraction of palladium, platinum and rhodium using Kelex 100 from HCl medium in absence and presence of tin. The extraction order was found to be reverse in the presence of tin. Demopoulos et al. (34) employed Kelex 100 for the extraction of Rh(III). Rh(III) showed quantitative extraction at a Sn(II)/Rh(III) ratio of ≥3 via the formation of Rh(III)-Sn(II)-Cl complex. Many other workers have also employed Kelex 100 for the extraction studies of platinum group metals (35-38).

Ohashi and researchers (39) studied the extraction behavior of Pd(II) using long-chain alkylated 8-quinolinol derivatives such as 5-dipropylaminomethyl-8-quinolinol (HN3Q), 5-dibutylaminomethyl-8-quinolinol (HN4Q), 5-propyloxymethyl-8-quinolinol (HQ3Q), 5-octyloxymethyl-8-quinolinol (HO8Q), and 2-methyl-5-octyloxymethyl-8-quinolinol (HMO8Q). They separated Pd(II) from other metal ions using HMO8Q and HO8Q. They also carried out the separation of Cu(II), Mo(VI), Pd(II), Ga(III), Co(II) and Ni(II) with 8-quinolinol derivatives.

Rane and Venugopal (40) used LIX- 84I to study the extraction and separation of Pd(II) and Pt(IV) in HCl medium. Palladium was extracted in the pH range of 1-3 while platinum beyond pH 8 in ammoniacal medium. The extractant forms a Pd-LIX complex with the stoichiometric ratio of 1:2. Stripping of palladium was achieved with 6 mol L^{-1} HCl and that of platinum with 3 mol L^{-1} HCl containing stannous chloride. Woollam and Grant (41) studied the degradation of ketoxime LIX 84I and the solvent extraction of palladium. They encountered the problem of slow phase separation caused by acid catalyzed degradation of the ketoxime by hydrolysis to the ketone. Reddy et al. (42) developed a process for the separation and recovery of palladium and platinum from spent automobile catalyst. Palladium from the leach liquor of spent catalyst was selectively extracted into a kerosene solution of LIX 84I followed by its stripping with acidic thiourea. Fe and Pt were then extracted with Alamine 336 and selectively recovered by scrubbing with HCl and acidic thiourea solution, respectively.

Utekar and co-workers (43) extracted Pd(II) using 2-oxo-4’-hydroxy-phenylacetaldehyde oxime from acetic acid medium. Effect of various phase parameters has been studied. Pd(II) was separated from other associated metal ions. Shen and Xue (44) employed 2-hydroxy-4-sec-octanoyl diphenyl-ketoxime for the separation of Pd(II), Au(III) and Pt(IV) from chloride medium. Selective stripping of Pd(II) and Au(III) from the loaded organic phase was achieved by varying acid molarity. Hassanien and Khaled (45) used a novel chelating ligand, 9,10-phenanthraquinone ethylthiosemicarbazone (PET), for the selective separation of Pd(II) by solid phase and liquid-liquid extraction from an acidic medium. Extractable species of Pd(II)-PET was found to be 1:1. Baba and coworkers (46) achieved high selectivity for Pt(IV), Au(III) and Pd(II) over associated metals like Co(II), Cu(II) and Ni(II) using toluene solution of N,N-Di(2-ethylhexyl)aminomethylquinoline (DEQ). They observed that Pt(IV) was extracted through the anion exchange and solvation mechanism, while Pd(II) by anion exchange mechanism only. Metal:Ligand ratio in extracting species for Pt(IV) was found to be 1:1 and 1:2 at low and high HCl concentration, respectively. Pd(II) was found to be extracted as a 1:1 complex. In the past various other types of oximes have been used for the extraction of platinum group metals by researchers (47, 48).

It is known that the use of chelating agents as extractants has radically declined due to some of their drawbacks like water solubility and the requirement of strict control of phase variables.

Amongst the different extractants used for the extraction and separation of PGMs, high molecular weight amines have also been employed by various groups of researchers. Kawano et al. (26) reported the extraction of platinum from hydrochloric acid medium using TOA diluted with toluene. The same research group investigated the extraction of Pt(IV) from HCl medium using toluene solution of TOA (27). The extracted metal was scrubbed employing NaOH solution. Balcerzak and Wyrzykowska

(49) performed extraction of platinum and ruthenium with TOA and diantipyrylmethane (DAM) in 1,2-dichloroethane diluent. Kolekar and Anuse (50) explored xylene solution of N-n-octylaniline for the extraction of rhodium from aqueous malonate medium. They reported that the time required for equilibration was 15 seconds only and quantitative stripping was achieved with different mineral acids. Levitin and Schmucker (51) employed tri-octyamine and Aliquat 336 for the separation of rhodium from palladium and platinum. Back extraction of rhodium was achieved with concentrated HCl.

Lee and his group (52) explored Aliquat 336 for the separation of platinum and rhodium. Separation factors of 279 and 612 were obtained for platinum and rhodium at 1.0 mol L^{-1} HCl and 3.0 mol L^{-1} HCl, respectively. The separation of Pt(IV) and Rh(III) using tri-iso-octylamine and Alamine 308 was also investigated by these researchers (53). The highest separation factor for Pt(IV) and Rh(III) was achieved with Alamine 308. LiCl was found to be a better salting-out reagent than other alkaline earth metal salts. The authors demonstrated the use of TBP and Aliquat 336 for the separation of palladium and platinum (54). A kerosene solution of Alamine 300 was used for the separation of platinum and palladium in the presence and absence of NaCl (55). Authors found that the addition of NaCl to the aqueous phase, decreased the extraction of palladium and accomplished selective stripping of platinum and palladium with sodium thiocyanate and sodium thiosulphate, respectively. Marinho et al. (56) tested various extractants namely Alamine 304, Alamine 336, Aliquat 336, DEHPA and TBP for the extraction of platinum. Aliquat 336 was found to be the best extractant for platinum. Platinum was quantitatively stripped using sodium thiosulphate, with simultaneous reduction from Pt(IV) to Pt(II).

Sun and Lee (57) tried various reagents for the stripping of platinum and palladium from the loaded Alamine 336. $HClO_4$ and Na_2CO_3 were found effective for the stripping of palladium and platinum, respectively. Neither HCl nor thiourea solution was effective for the stripping of the two metals. However, a mixture of HCl and thiourea greatly enhanced the stripping power. The same group carried out studies to achieve separation of platinum from iron and aluminium using both solvent extraction and ion exchange (58). For solvent extraction studies, Alamine 304-1, Alamine 308, Alamine 336, Aliquat 336, TBP and TOPO were investigated as extractants, while AG1-x8 resin was employed for ion exchange studies. They concluded that it was difficult to separate platinum from iron and aluminium by the proposed solvent extraction method whereas most of the platinum was loaded onto the ion exchange resin leaving behind iron and aluminium. They also optimized the conditions to separate rhodium and iridium from chloride solution using Alamine 336 and TBP (59). Effects of extraction conditions on the separation of both the metals were investigated. Extraction order of rhodium and iridium was changed by adding $SnCl_2$ to the mixed solution. It was further observed that the highest separation factor was obtained with Alamine336 in the presence of $SnCl_2$. Jaree and Khunphakdee (60) investigated Pt-Rh separation in chloride medium using tri-octylamine in toluene. Platinum was selectively stripped with 8 mol L^{-1} HNO_3. They concluded that soyabean oil can be used as a substitute for toluene, with good extraction performance comparable to that of toluene.

Although, HMWA have been extensively used for the extraction and separation of PGMs but they suffers from some limitations. The most usually encountered problems with long chain alkylamines are of emulsion formation and poor selectivity. Thus it would not be wrong to say that as now organophosphorus compounds are more or less dominating the market of extractants and with the passage of time various types of compounds namely alkylphosphoric, -phosphonic, - phosphinic acids, their esters, phosphine oxides and their sulphur analogues have become available. Abundant literature is available on the use of these reagents for analytical separations of closely related elements and their use in hydrometallurgy. The first compound of this class to be used extensively was TBP and subsequently DEHPA and TOPO gained prominence. Amongst the esters of phosphoric acid, di-(2-ethylhexyl) phosphoric acid (DEHPA) has by far received maximum attention for the distribution studies of various groups of metals but to the best of author’s findings practically no literature regarding solvent extraction of PGMs using DEHPA has been reported.

Till about 1980 not many organophosphorus compounds were available as commercial extractants and their sulphur analogues were practically unknown to metal extraction chemists. The real breakthrough in the solvent extraction chemistry of metals came with the introduction of some alkylphosphinic acids, alkylphosphine oxides and their sulphur analogues by American Cyanamid Company, USA (now

Cytec Canada Inc., Canada) under the trade name of ‘CYANEX’. It included alkylphosphinic acid namely, bis(2,4,4-trimethylpentyl) phosphinic acid (Cyanex 272), its sulfur analogues, bis(2,4,4-trimethylpentyl) monothiophosphinic acid (Cyanex 302) and bis(2,4,4-trimethylpentyl) dithio phosphinic acid (Cyanex 301), two alkylphosphine oxides Cyanex 923 (a mixture of straight chain alkylphosphine oxides) and Cyanex 925 (a mixture of branched chain alkyl phosphine oxides in 85:15 ratio) and a phosphine sulfide (Cyanex 471X). About the same time the company also marketed the formulation of tri-n-octylphosphine oxide (TOPO) under the product name ‘Cyanex 921’. Cyanex 923 is a mixture of four alkylphosphine oxides and its performance is rated to be much better than TOPO because it is a liquid with low freezing point and is completely miscible with all commonly used hydrocarbon diluents even at low ambient temperatures. Cyanex 471X (triisobutylphosphine sulphide – TIBPS) is a sulphur analogue of a phosphine oxide. Because of a lower pKa value it is able to extract metal ions at a higher acidity than TOPO. These reagents differ from other kinds of organophosphorus extractants in the manner that the alkyl groups are bonded directly to the phosphorus atoms through P-C bond rather than P-O-C bonding. This makes phosphine derivatives less water soluble and more resistant to hydrolysis, which thereby mitigates the problems of emulsion formation and reagent loss. The organophosphorous extractants need special attention because they can act as both, a cation exchanger and a solvating molecule.

The inherent advantages of the organophosphorus extractants fascinated the research community to explore them for the separation and recovery of various metal ions. In the last twenty-five years, there has been a phenomenal growth of literature on these organophosphorus extractants. In a search for a better extractant for PGMs, as a first step, the existing information on the use of organophosphorus compounds for these elements was reviewed and is briefly presented in the following few pages.

Kedari and co-workers (30) employed a number of commercial extractants for the separation of iridium, ruthenium and rhodium from HCl medium. The extractants studied were Alamine 300, Alamine 336, Aliquat 336, Cyanex 921, Cyanex 923, Cyanex 471X, Lix 54, Lix 860N-I and tri-butyl phosphate. Nejad and Kazemein (31) investigated the effect of alkaline metal salts on the solvent extraction of platinum from leached spent dehydrogenation catalysts (Pt/Al_2O_3) in aqua regia by the trioctylphosphine oxide (TOPO). Best salting out effect was achieved with KCl as the additive salt. It was found that the extraction of platinum by TOPO was kinetically fast and the required equilibrium time was less than 30 seconds. Mhaske and Dhadke (61) studied the extraction of rhodium, platinum and palladium using Cyanex 921 from chloride medium in the absence and presence of tin chloride. Effect of different phase variables has been studied. The developed method was employed to recover the PGMs from synthetic mixture. From the same laboratory the distribution of Pt(IV) from HCl medium using toluene solution of Cyanex 921 and Cyanex 925 were carried out (62). The extractable species were $(H^+\text{-}2R)_2PtCl_6^{2-}$, where R stands for the extractant. The same group explored Cyanex 921 for the extraction of Os, Ru and Ir from chloride medium in the absence and presence of $SnCl_2$. Effect of various parameters was studied (63). The reported method was applied to the recovery of PGMs from catalyst samples. Ma et al. (64) used TOPO for the separation of Rh(III) and Ir(IV) from tin chloride medium. A study on the extraction of rhodium into TOPO has also been reported by Ma et al. (65). The effect of various phase parameters was studied. Quantitative stripping was achieved with acidic solution of potassium chlorate.

In one of the reports Cyanex 925 has been explored for the separation of Os(VIII), Ru(IV) and Ir(III) from chloride medium in the absence and presence of tin chloride (66). The separation of individual metal ions was achieved by selective extraction/stripping. The proposed methods were applied for the recovery of these metal ions from some real catalyst samples. The same authors used Cyanex 925 to investigate the extraction of Rh(III), Pt(IV) and Pd(II) from chloride medium in the absence and presence of $SnCl_2$ (67). In the absence of tin (II) chloride, the order of extraction was found to be Pd > Pt > Rh. However, in the presence of tin (II) chloride, it changed to Pt > Rh and is negligible in the case of palladium.

Apart from the use of various alkyl phosphine oxides, Cyanex 301 and Cyanex 302 have also been explored for the extraction of PGMs. Kakoi and group (68) studied the extaction of palladium using n-heptane solution of Cyanex 301 and Cyanex 302. The stoichiometric ratio was found to be 1:1 and 1:2 for Cyanex 301 and Cyanex 302, respectively. Thiourea was used as a stripping reagent. Sarker and Dhadke (69) reported the extraction of Pd(II) from chloride medium using toluene solution of Cyanex 302. Effect of various parameters namely acid and extractant concentration, equilibration time and effect of foreign ions was studied. The method was simple and fast and separated Pd(II) from closely associated metal ions. Kumar and associates (70) investigated the extraction of Pt(IV) from chloride, sulphate and nitrate media using Cyanex 302. The extraction of Pt(IV) increased with the increase in the extractant concentration in the order sulphate > chloride > nitrate. The extraction behavior of iron, copper, silver, aluminum, magnesium and calcium was also studied. The same group studied the extraction of Pt(IV) with kerosene diluted Alamine 336 and Cyanex 302 from HCl medium (71). Effect of different parameters has been studied. Gore and group (72) reported the extraction of Rh(III) using chloroform solution of Cyanex 301 from chloride medium in the presence of $SnCl_2$. Effect of various parameters was studied. They concluded that the method was simple, fast and sensitive and separation of Rh(III) from metal ions like Cu(II), Co(II) and Mn(II) was achieved. Studies have also been conducted on the use of Cyanex 301 and Cyanex 302 for the extraction of PGMs by supercritical fluid extraction, reactive precipitation and adsorption methods (73-76).

In the light of literature reviewed by the author it is evident that DEHPA has not been explored for PGMs and only a few reports are available on the use of Cyanex 923 and Cyanex 471X for the extraction and separation of PGMs. Thus it was planned to explore Cyanex 923, Cyanex 471X and DEHPA for the separation and recovery of the PGMs. Osmium was not considered for the studies, as among PGMs osmium finds least application in the race of development. Literature regarding these three extractants with reference to various metal ions including PGMs is reviewed in the respective chapters. It may be important to point out here that the scenario with regard to the availability of PGMs in India is no better than most of the developing nations. Needless to say that for meeting the demand and supply gap of the country efficient indigenous methods has to be developed to recover these metals from secondary sources. The Council of Scientific and Industrial research (CSIR), New Delhi, India sponsored us a research project to develop liquid-liquid extraction methods to recover the said metals from spent matrices.

As a first step the extraction behavior of Pt(IV), Ir(III), Rh(III), Ru(III) and Pd(II) has been investigated in Cyanex 923, Cyanex 471X and DEHPA from different acid media. Along with PGMs, the distribution of associated metal ions such as Au(III), Fe(III), Cr(III), Al(III), Cu(II), Ni(II), Co(II), Fe(II) and Ag(I) has been studied. The studied associated metal ions are likely to be encountered with PGMs in different matrices. The extraction behaviour of associated metal ions was investigated only from the media in which the PGMs exhibited maximum extraction.

In order to investigate the stoichiometric ratio of the extracting species and optimize the conditions for different separation parameters like equilibration time, temperature, nature of diluent, type of mineral acid and concentration of the acid and extractant have been studied. The probable stoichiometric ratios of the extracting species have been identified. The partition data obtained under varying experimental parameters offered conditions for binary separations involving the said PGMs. The proposed separation steps have been fused together to develop separation schemes for the recovery of some PGMs from different matrices like catalyst standard, spent Pt-Rh thermocouple wire, coated ceramic honeycomb and palladium coated alumina catalyst. In order to assess the practical utility of the proposed system some properties of the extractants like loading capacity, stability towards prolonged contact with acid and regeneration capacity have been checked.

After the detailed liquid-liquid extraction studies on some PGMs, it was logical to extend the use of organophosphorus extractant for permeation studies by membrane based extraction technique. As a representative case Cyanex 923 was employed as a carrier for permeation studies on Pd(II) using flat sheet supported liquid membrane (FSSLM). The operational parameters were optimized for the ease and rapid permeation of Pd(II) through Cyanex 923 impregnated FSSLM. In order to assess the recycling capacity and stability the liquid membrane technique was subjected to several successive permeation cycles and long term acid contact with feed as well as receiving phases.

For the convenience of presentation and to maintain clarity, the present thesis is indexed in the following five chapters, I Introduction.

II Materials, Equipments And Methodology.

IIIA Extraction Studies on Pt(IV), Rh(III), Pd(II) And Associated Metal Ions Using Cyanex 923 .

IIIB Permeation Studies on Pd(II) Using Supported Liquid Membrane Impregnated With Cyanex 923.

IV Extraction Studies on Pt(IV), Ir(III), Rh(III) And Associated Metal Ions Using Cyanex 471X

V Extraction Studies on Pt(IV), Ir(III), Rh(III) And Associated Metal Ions Using DEHPA

The thesis ends with a brief discussion on the findings of the present investigations in the form of conclusions. The contents of each chapter have been summarized in the accompanied abstract of the thesis.

Utmost care has been taken in compiling the relevant literature. However, some important contributions might have been omitted by an oversight, non-availability of information or error in judgment. Hence, the author would like to apologize for such an omission, if any. In presenting the work due attention has been paid to avoid repetition. However, at times it has not been possible to do so in order to maintain the continuity and clarity in the text.

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CHAPTER II

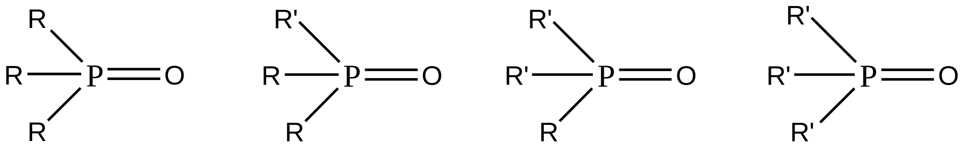
MATERIALS, EQUIPMENTS AND METHODOLOGY

1. Materials

Chlorides / nitrates / sulphates of platinum(IV), iridium(III), rhodium(III), ruthenium(III), gold(III), chromium(III), iron(III), aluminium(III), palladium(II), copper(II), nickel(II), cobalt(II), iron(II) and silver(I) were analytical grade materials from Sigma-Aldrich (USA) / BDH (UK) / E.Merck (Germany) / Thomas Baker (India). All other chemicals and solvents used were of G.R. / Synthesis grade from E. Merck. Kerosene (160 – 200°C), with 65 – 75 % aliphatic and 25 – 35 % aromatic fractions was used.

Stock solutions of the different metal ions were prepared by dissolving their salts in ultra pure water containing a minimum concentration of the corresponding mineral acid. These solutions were standardized by complexometric titration methods reported elsewhere (1).

Cyanex 923 and Cyanex 471X were received as gift samples from Cytec Canada Inc., Canada, and DEHPA was procured from Merck and were used without further purification. Cyanex 923 contained trialkylphosphine oxides namely dioctyl-hexylphosphine oxide, dihexyl-octylphosphine oxide, trihexylphosphine oxide and trioctylphosphine oxide. The structures and percentage of the different constituents are given as follows.

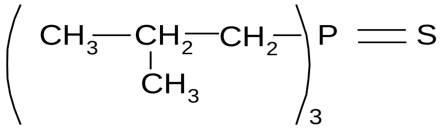


(~8%) (~32%) (~42%) (~14%)

[Cyanex 923]

R = CH_3-$(CH_2)_5$-, R' = CH_3-$(CH_2)_7$-

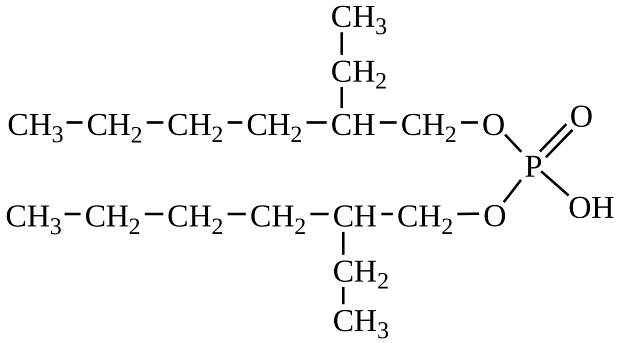
The active ingredient of Cyanex 471X is triisobutylphosphine sulphide (TIBPS). The chemical structure of Cyanex 471X is as given below



$$\left(CH_3-\underset{CH_3}{\underset{|}{CH_2}}-CH_2-\right)_3P=S$$

[Cyanex 471X]

Di-(2-ethylhexyl)phosphoric acid (DEHPA or HDEHP) is a diester of phosphoric acid and 2-ethylhexanol. Molecular formula of DEHPA is $(C_8H_{17}O)_2PO_2H$.



[DEHPA]

The average molecular weights of Cyanex 923, Cyanex 471X and DEHPA are taken to be 348, 237.4 and 322.42. The extractant solutions were prepared by diluting them to a known concentration with an appropriate organic solvent. The extractants were used as supplied unless reported.

2. CATALYST STANDARD, SPENT THERMOCOUPLE WIRE, COATED CERAMIC HONEYCOMB AND Pd/Al_2O_3 CATALYST

Catalyst standard (NIST SRM-2556) was procured from NIST. Pt-Rh thermocouple was collected from electrical repair workshop, Roorkee, Uttarakhand. The sample of coated ceramic honeycomb was obtained from SUD-CHEME Pvt. Ltd., Vadodara, Gujarat (India). Spent palladium coated alumina catalyst was received from Indian Institute of Petroleum (IIP), Dehradun, Uttarakhand (India). The different samples listed above were used for the recovery of platinum, palladium and rhodium.

3. EQUIPMENTS

The distribution studies for metal ions and analysis of digested matrix solutions were carried out using an Atomic Absorption Spectrometer, AAS (AAnalyst 800, Perkin Elmer, Germany) or Inductively Coupled Plasma – Optical Emission Spectrometer, ICP-OES (Perkin Elmer, Germany). The calibration of ICP-OES was performed by sequential on peak measurement of the corresponding emission signal and background. Prior to the analysis of metal ions on AAS/ICP-OES calibration plots were drawn using closely matched standards. A temperature controlled (±0.1^{o}C) shaking water bath (Julabo, Germany) was used to study the effect of temperature on the partition of metal ions. The pH measurements were made by a digital pH meter (Model PH-102, Lutron, Taiwan). The pH meter was standardized by standard buffer solutions of known pH. For distribution studies, a mechanical shaker (Riviera, Bombay, India) was used to agitate the liquid-liquid phase for pre-determined time intervals. The membrane permeation experiments were conducted on a two compartment methacrylate permeation cell with a groove in between to hold the membrane. Each cell had a dimension of 10.3 x 10^{2} cm^{3}.

4. EXPERIMENT

4.1. Extraction Procedure

The distribution studies were carried out by contacting mechanically equal volumes of the aqueous (metal ion solution containing an appropriate molarity of the acid) and the organic (solution of Cyanex 923/471X and DEHPA in an appropriate organic solvent) phases at room temperature (25±3^{o}C) for six minutes to ensure complete equilibration. After clear separation of both the phases the concentration of the metal ion in aqueous phase before and after distribution was analyzed by ICP-OES/AAS. The metal ion concentration in the organic phase was calculated by mass balance as below

$$C_{organic} = C_{aqueous\ before\ extraction} - C_{aqueous\ after\ extraction}$$

The distribution ratio and percentage of extraction were calculated using the following expressions

$$\text{Distribution ratio (D)} = [\text{Metal}]_{Organic} / [\text{Metal}]_{Aqueous}$$

[1]

Percentage extraction (%E) = $[\text{Metal}]_{\text{Organic}} / \{[\text{Metal}]_{\text{Aqueous}} + [\text{Metal}]_{\text{Organic}}\} \times 100$ [2]

The effect of equilibration time on the partition of the metal ion was investigated by shaking the aqueous and organic phases for different time intervals. For studying the effect of diluents on the distribution of various metal ions, Cyanex 923/Cyanex 471X/DEHPA were diluted with solvents of different dielectric constant and used as the organic phase. To study the effect of temperature on the partition of different metal ions distribution studies were carried out at different temperatures keeping the other experimental parameters constant. The enthalpies of extraction were calculated using Van't Hoff equation $-\ln K_{ex} = \Delta H/R \times 1/T$, K_{ex} is extraction constant. The investigations on the extraction behaviour of different metal ions were carried out by taking an individual metal ion in the aqueous phase.

Wherever necessary the acidity of the aqueous phase was lowered either by dilution or evaporating the excess of the acid. The exact experimental conditions for various studies have been indicated along with the corresponding data.

4.2. Permeation Studies

In the membrane-based extraction studies, the hydrophobic Pal's FluoroTrans® polyvinylidene fluoride (PVDF 1015) transfer membrane was used as a supporting medium. The physical characteristics of the hydrophobic PVDF membrane support are summarized in Table 1.

The value of the tortuosity (τ) was calculated according to the relationship:

$$\tau = (1+V_p) / (1-V_p) \quad [3]$$

where, $V_p = 1-\varepsilon$ is the volume fraction of the polymeric framework (2).

Table 2.1 Characteristics of the transfer membrane used in the permeation studies

Membrane Support	*Membrane Thickness D_{org} (μm)*	*Membrane Porosity ε (%)*	*Membrane Tortuosity τ*	*Membrane pore size (μm)*
FluoroTrans® PVDF Transfer Membrane	127	75	1.67	0.2

4.3 Stripping

Stripping of the extracted metal ion from the loaded organic phase was carried out by equilibrating the loaded organic phase with single or multiple volumes of the stripping phase keeping the aqueous to organic phase ratio constant at unity unless otherwise mentioned. In some cases the back extraction of different metal ions from the same organic phase was achieved by selective stripping.

4.4 Stability and Regeneration Capacity of Extractant

The stability of toluene solutions of Cyanex 923, Cyanex 471X and DEHPA was checked by keeping them in contact with 6.0 mol L^{-1} acid for 50 days with intermittent shaking. A known volume of the organic phase was separated periodically after five days and used for the extraction of the respective metal ion after washing with water.

The regeneration capacity of the extractants was investigated by carrying out successive extraction-stripping cycles for a metal ion employing the same organic phase repeatedly. In between each cycle the extractant phase was washed with water till the washings were nearly neutral.

4.5 Dissolution of real samples

The samples of catalyst standard (NIST SRM-2556), spent Pt-Rh thermocouple wire, spent palladium coated ceramic honeycomb, spent palladium coated alumina catalyst, were dissolved/leached using appropriate methods. The type, volume and molarity of the acid were optimized to match the conditions of separations. In order to get representative data three different samples of each of the matrices were processed. The detailed procedures followed for the preparation of stock solutions of different samples are given in the following text.

(a) Catalyst standard (NIST SRM-2556)

About 1 g of the powdered standard sample was digested with 12 mL HF, 24 mL HNO_3 and 12 mL of $HClO_4$ in microwave digestion system, and the resulting solution was evaporated to near dryness. The residue was again boiled to near dryness with 10 mL of 2 mol L^{-1} HNO_3. . The procedure was repeated thrice. The residue was then dissolved with 10 mL of 5.0 mol L^{-1} H_2SO_4 by heating gently on a hot plate. The resulting solution was then cooled, filtered and made up to 25 mL adjusting the acidity to 5.0 mol L^{-1} H_2SO_4 and designated as [S1]. The aqueous solution [S1] containing platinum(IV), rhodium(III) and palladium(II) was used to validate the proposed separation scheme.

(b) Pt-Rh thermocouple wire

About 1 g Pt-Rh thermocouple wire was digested twice with 15 mL of concentrated HCl to dissolve platinum. This was followed by digestion with 15 mL of concentrated H_2SO_4 to dissolve rhodium. The solution was heated to near dryness with 10 mL of 2 mol L^{-1} $HNO_{3.}$ The procedure was repeated thrice and the final acid concentration was adjusted to as per the requirement in 10 mL of solution. This solution was marked as [T1] and used for the recovery of platinum and rhodium.

(c) Palladium coated ceramic honeycomb

Coated ceramic honeycomb containing Pd and Rh was crushed to fine powder. About 1 g of the powdered sample was digested with 15 mL HF, 7 mL HNO_3 and 7 mL of $HClO_4$ in microwave digestion system, and evaporated to near dryness. The residue was again boiled to near dryness with 10 mL of 2 mol L^{-1} $HNO_{3.}$ The procedure was repeated thrice. The residue was then dissolved in 10 mL of 5.0 mol L^{-1} H_2SO_4 by heating gently on a hot plate. The resulting solution was then cooled, filtered and made up to 25 mL adjusting the acidity to 5.0 mol L^{-1} H_2SO_4. This solution was marked as [H1] and used for the recovery of palladium and rhodium.

(d) Palladium coated alumina catalyst

About 0.25 g of finely powdered spent catalyst was kept in contact with 10 mL of 12.0 mol L^{-1} sulphuric acid for four days. The leached solution was then filtered and diluted to 25 mL keeping over all acidity to 5.0 mol L^{-1} H_2SO_4. This solution was marked as [C_1] and used for the recovery of palladium. It was checked that keeping the powdered spent catalyst sample in contact with H_2SO_4 for ten days did not enhance the amount of palladium leached out.

The composition of the sample solutions with respect to the concentration of metals of interest in samples and the procedures for their recovery are given in the respective chapters. The percentage recovery and purity of metals separated were calculated using the following expressions -

$$\text{Percent Recovery} = \{[\text{Desired Metal}]_{\text{Recovered}} / [\text{Desired Metal}]_{\text{Initial}}\} \text{x } 100 \qquad [4]$$

$$\text{Percent Purity} = \{[\text{Desired Metal}]_{\text{Recovered}} / [\text{Total Metals*}]_{\text{Recovered}}\} \text{x} 100 \qquad [5]$$

where [Total metals*] refers to metals for which the solution was assayed.

5. STATISTICAL ANALYSIS OF DATA

The different results reported in the thesis are based on a minimum of two determinations. Blank determinations were carried out wherever necessary and the corrections were carried made if required. To give an idea of the precision of the data the standard deviation was calculated as follows

$$\text{Standard Deviation } (\sigma) = \pm\sqrt{}(X_{\text{observed}} - X_{\text{mean}})^2 / N \qquad [6]$$

where N = Total number of observations.

The values of standard deviation for the data given in the tables are indicated along with the corresponding results. The standard deviation for the data plotted in different figures has been indicated in the form of y-error bars. However, sometimes the value of standard deviation is too small to be legible in the plot. In different log-log plots the values of standard deviations are invariably very small (0.0 – 0.3) and not shown in the figures.

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CHAPTER IIIA

EXTRACTION STUDIES ON Pt(IV), Rh(III), Pd(II) AND ASSOCIATED METAL IONS USING CYANEX 923

The interest in the synthesis and development of various extractants has always been on an escalating rise and it is difficult to keep pace with the developments in this field. Over the years different types of compounds have been used as extractants for the metals. The application of a large number of them is restricted up to the bench level. The real breakthrough in the liquid-liquid extraction chemistry of metals came with the introduction of some new commercial extractants by Cytec Canada Inc., Canada under the trade name of Cyanex.

In the nineties of twentieth century Cyanex 923 has gained prominance as an extractant for various metal ions. Cyanex 923, a mixture of four straight chain trialkyl phosphine oxides namely, $R_3P{=}O$, $R'R_2P{=}O$, $R'_2RP{=}O$, $R'_3P{=}O$, R is n-octyl and R' is n-hexyl has proved to be more versatile and promising because of some of its inherent advantages. It is a liquid with low freezing point and is completely miscible with most of the commonly used diluents and can be used at high concentration even at low ambient temperatures. It has low aqueous solubility and good recycling capacity. Moreover, Cyanex 923 offers a quicker phase separation (1). An idea about its increasing popularity can be had from the literature, citing its utility for the separation and recovery of various metal ions.

At earlier stages of its development Cyanex 923 was used for the recovery of phenols, acetic acid and ethanol (2). Rickelton (3) emphasized the importance of Cyanex 923 for the recovery of mineral acids. Alguacil and Lopez (4) also studied the distribution of mineral acids such as H_2SO_4, H_3PO_4, HCl, $HClO_4$ and HNO_3 in Cyanex 923. Cziwinski and Szymanowski (5) studied the composition of Cyanex 923 along with few other extractants. Cyanex 923 contained 18 components, out of which seventeen were identified (92.4 %) as trialkylphosphine oxides, mainly with normal hexyl and octyl groups.

Sahu and coworkers (6) used xylene solution of Cyanex 923 for the extraction of U(VI) and Th(IV) from nitrate medium. The compositions of the extracted species were deduced by slope analysis and IR studies. The selectivity of Cyanex 923 for these metal ions was evaluated and compared with that of the other commercial extractants. Xiaogui and Chongli (7) used kerosene solution of Cyanex 923 for the extraction of

Tc(VII) from nitric acid medium. The effect of concentration of HNO_3 and Cyanex 923 and the temperature on the extraction of Tc(VII) was investigated. Dietz and associates (8) proposed an improved extraction chromatographic method for the separation of uranium from acidic nitrate medium and found Cyanex 923 to be better than Cyanex 925 due to its lower viscosity and higher selectivity for U(VI) over Fe(III).

Plenty of work on the extraction of various metal ions employing this extractant is reported from author's laboratory. The extraction of uranium, thorium and lanthanides by Cyanex 923 has been examined (9). The composition of the extracted U(VI) and Th(IV) species were proposed and some important binary and ternary separations were carried out. The proposed procedure was applied for the recovery of U(VI), Th(IV) and lanthanides from monazite sand. The stability and regeneration capacity of the extractant was evaluated. In another publication Gupta et al. (10) investigated the extraction behavior of some tervalent lanthanides along with Y(III) from HCl, HNO_3, H_2SO_4 and H_3PO_4 media in toluene solution of Cyanex 923. The effect of equilibration time, nature of diluent and concentration of acid, extractant and metal ion on the extraction was investigated. The authors separated lanthanides into four fractions. The method was successfully employed for the separation of lanthanides and yttrium from a synthetic mixture in different fractions.

Investigations on the extraction and stripping of ytterbium(III) from sulphate medium using heptane solution of Cyanex 923 were conducted by Weiwei et al (11). It was found that the extraction of Yb(III) from sulphate medium by Cyanex 923 increased with pH, concentration of sulphate and bisulphate ion and extractant. A quantitative extraction of Yb(III) was achieved at pH 3, and the extracted species was found to be $YbSO_4(HSO_4)$.2Cyanex923. El-Nadi (12) carried out extraction of Pr(III) and Sm(III) with Cyanex 923 in various diluents from nitrate medium. His findings illustrated that with increasing dielectric constant of the diluent, the extraction percent decreased. On the basis of slope analysis, the composition of the extracted species was determined as $M(NO_3)_3$.2Cyanex 923. Many other research groups have also employed Cyanex 923 for distribution studies on lanthanides (13-20).

Cox and group (21) compared Cyanex 923, LIX 1104 and Acorga SBX 50 for the removal of impurities like As, Sb and Bi from copper electro refinery electrolytes and found Cyanex 923 to be most effective. Wang et al. (22) also reported Cyanex 923 as an effective extractant for the purification of copper electrolytes. They proposed a novel process involving extraction with Cyanex 923 followed by subsequent adsorption on activated carbon for the recovery of As, Sb and Bi. From the author's laboratory a study on the extraction of In(III) and the associated metal ions from HCl, H_2SO_4 and HNO_3 media using toluene solution of Cyanex 923 (1) has been carried out. The stochiometry of the extracting species was observed to be 1:2 (metal:extractant). Effect of different phase variables like concentration of extractant, acid and metal ion on the extraction of indium was studied. Based on the partition data conditions were identified for attaining some binary separations of In(III). The conditions were extended for the recovery of pure indium from zinc blende, zinc plating mud and galena. The same group explored Cyanex 301/Cyanex 923 for the separation of Ge(IV) from commonly associated metal ions (23). The extractable species was identified as $GeCl_4$.2R, where R is extractant. The data obtained was extended to develop a scheme for the recovery of Ge(IV) from semiconductor waste. Gupta et al. (24) also investigated the extraction behavior of Ga(III) and associated metal ions from HCl medium using Cyanex 923. Effect of different parameters has also been investigated. The extracting species has been identified as $GaCl_3$.3Cyanex 923. The developed separation conditions have been utilized to recover Ga(III) from light emitting diode (LED) waste and bottom ash. Research group of Ahmed (25) explored Cyanex 923 and Cyanex 925 for the extraction of Ga(III) from chloride medium. The stripping was found to be efficient with 1 mol L^{-1} HCl. The findings indicated the possibility of the separation of Ga(III) from interfering ions, namely Zn(II) and Cu(II).

A fair volume of literature is reported regarding the use of Cyanex 923 for the distribution studies of transition metal ions. Meera et al. (26) investigated the extraction of Hg(II) from HCl medium using xylene solution of Cyanex 923. The results demonstrated that Hg(II) was extracted as $HgCl_2$.3Cyanex 923. The developed extraction procedure was explored for the recovery of mercury from the brine-sludge of Chlor-Alkali industry. Gupta et al. (27) used Cyanex 923 for the recovery of cobalt and nickel from spent catalysts. In another report (28), they explored Cyanex 923 for the extraction and separation of some 3d transitional metal ions namely Ti(IV), V(IV), Cr(III), Fe(III), Mn(II), Co(II), Ni(II), Cu(II) and Zn(II). The effect of some important parameters such as the concentration of extractant and metal ion and the nature of diluents on the partition was investigated in detail. Based on the distribution data some binary separations of analytical interest were achieved. The same group studied the recovery of chromium and nickel from different industrial wastes, namely, Cr(III)-Ni(II) plating sludge, Ni(II) plating mug and a tannery effluent (29). The proposed methods employed precipitation, solvent extraction and electrowinning steps. In another publication (30) of the same group, selective extraction of cobalt using toluene solution of Cyanex 923 has been studied. The extraction of Zr(IV) using toluene solution of Cyanex 923 has also been investigated (31). Effect of various parameters on the partition of Zr(IV) was studied. The stoichiometry of the extracted species was found to be 1:1. The data was utilized to recover Zr(IV) from multi-element mixtures.

Deep and group (32) proposed the separation of Fe(III) and Cr(III) using Cyanex 923. Fe(III) was extracted in Cyanex 923 by forming a complex $FeCl_3$.2Cyanex 923. The partitioning of Fe(III) in the organic phase was selective over Cr(III) with its kinetics being reasonably fast. The developed method was used to separate and recover Fe(III) and Cr(III) from tannery filtrate. Sarangi et al. (33) demonstrated the separation of Fe(III), Cu(II) and Zn(II) using kerosene solution of TBP, LIX 84I and Cyanex 923, respectively. Iron, copper and zinc from loaded TBP, LIX 84I and Cyanex 923 were stripped with water, sulphuric acid and water, respectively. Agarwal and coworkers (34) studied the removal of Cr(VI) from chloride solution using Cyanex 923 diluted with kerosene. The extracted Cr(VI) was quantitatively stripped with 1 mol L^{-1} NaOH. It was reported that the percent extraction of Cr (VI) decreases with the increase in temperature. The interference of the impurities usually associated with Cr(VI) such as Cr(III), Cu(II), Ni(II), Fe (II), Zn(II), chloride and sulphate were examined under the optimized conditions and only zinc was found to interfere. Taghizadeh (35) employed the mixture of TBP and Cyanex 923 for the separation of zirconium and hafnium. The effect of TBP/Cyanex 923 volume ratio, concentration of nitric acid, $NaNO_3$ and extractant on the distribution of zirconium and hafnium has been studied. Many other publications (36-45) are also available employing Cyanex 923 for the extraction of various transitions metal ions.

Among precious metals the extractant has been mainly explored for gold and some platinum group metals. Alguacil and group (46) studied the partition of gold between aqueous cyanide solutions and organic phases of the mixture of the amine Primene JMT and Cyanex 923 in xylene. The probable extractable species was found to be $HAu(CN)_2RNH_2(R_3PO)_n$, where n was 1 or 2. Gold was stripped using NaCN or NaOH. Martinez and others (47) reported the extraction of Au(III) from HCl medium using Cyanex 923. Different phase variables have been studied. Based on the data they explained the formation of $HAuCl_4L_2$ species in the organic phase. A few other studies reporting the use of Cyanex 923 for the liquid-liquid extraction of Au(III) are also cited in the literature (48-50).

Only a few reports are available on its use for the extraction of some platinum group metals. Kedari et al. (51) recovered Ir(III) and Ru(III) from chloride solutions using Cyanex 923 (C923) dissolved in kerosene. The organometallic species extracted in the organic phase were elucidated to be a mixture of $IrCl_4$.2C923-$HIrCl_5$.C923 and $HRuCl_4$.C923 for Ir(IV) and Ru(III), respectively. Ir was quantitatively stripped with distilled water and Ru using ascorbic acid. Another group carried out distribution studies on Ru(III) from chloride medium using TBP and Cyanex 923 (52). Cyanex 923 resulted in higher percent extraction of Ru(III) than TBP. Dhadke et al. used Cyanex 923 for the extraction of PGMs from aqueous bromide (53, 54) and hydrochloride medium using tin chloride as a labilising agent (55). The use of HBr and $SnCl_2$ may not be convenient for commercialization of the process.

The ongoing discussion highlights the emerging interest towards the recovery of Pt(IV), Rh(III) and Pd(II) from different types of leaner sources. The literature survey on the use of Cyanex 923 have established itself as a well known extractant with several inherent advantages and it may be prudent to use it for the said purpose. Keeping this in mind it was planned to carry out studies on the extraction of Pt(IV), Ir(III), Rh(III), Ru(III) and Pd(II) in Cyanex 923 from $HCl/H_2SO_4/HNO_3$ medium. The effect of variables such as equilibration time, temperature, nature of diluent and concentration of acid and extractant on the partition of Pt(IV) and Pd(II) has been investigated. Based on the distribution data the stoichiometries of the extracting species have been identified and loading capacity of the extractant assessed. Suitable stripping reagents for the metal ions have been worked out. The extraction behavior of some associated metal ions namely Au(III), Fe(III), Cr(III), Al(III), Cu(II), Ni(II), Co(II), Fe(II) and Ag(I) in Cyanex 923 from different mineral acid media has also been examined. The partition data on different metal ions has been utilized to achieve a number of binary separations. The optimized experimental conditions have been extended for the recovery of Pt(IV), Rh(III) and Pd(II) from standard catalyst, thermocouple wire, ceramic coated honey comb and palladium coated alumina catalyst.

Results and Discussion

The following text highlights the extraction behavior of Pt(IV), Ir(III), Rh(III), Ru(III), Pd(II) and other associated metal ions in Cyanex 923.

Extraction behavior of Pt(IV), Ir(III), Rh(III), Ru(III) and Pd(II) from different acids using 0.10 mol L^{-1} toluene solution of Cyanex 923

Figures 3A.1, 3A.2 and 3A.3 depict the extraction behaviour of Pt(IV), Ir(III), Rh(III), Ru(III) and Pd(II), respectively, from HCl, H_2SO_4 and HNO_3 media (0.10 to 6.0 mol L^{-1} acid) using 0.10 mol L^{-1} Cyanex 923 solution in toluene. Pt(IV) shows ~70% extraction at 0.10 mol L^{-1} HCl which remains constant up to 0.50 mol L^{-1} HCl and thereafter increases to attain a maximum value of almost 100%. However, from H_2SO_4 medium the maximum extraction (~55%) of Pt(IV) is obtained at 2 mol L^{-1} and decreases on increasing or decreasing acid concentration. In HNO_3 medium maximum extraction of Pt(IV) (~55%) is achieved between 0.10 and 0.50 mol L^{-1} HNO_3 and thereafter decreases slightly. Ir(III) shows the minimum extraction (~35%) at 0.10 mol L^{-1} HCl and increases with increasing acidity and becomes maximum (~88%) at 6.0 mol L^{-1} HCl. From sulphate medium the percent extraction of Ir(III) is constant in acid range from 0.10 to 1.0 mol L^{-1} H_2SO_4 but beyond this a decrease is observed and attains a minimum value (~15%) at 6.0 mol L^{-1} H_2SO_4. From HNO_3 medium Ir(III) exhibits 46% extraction at 0.10 mol L^{-1} HNO_3 which increases up to 2.0 mol L^{-1} HNO_3 and then remains constant at high acid molarity.

Rh(III) shows negligible extraction from chloride and sulphate media. However, from nitrate medium Rh(III) shows a maximum extraction of ~20% at low acidity and decreases with the increasing acidity to attain a negligible value. The extraction of Ru(III) remains almost constant (10-40%) in all the three mineral acids in the investigated range of acid molarity. The maximum extraction (~40%) of Ru(III) is observed at 0.10 mol L^{-1} HCl. The extraction of Pd(II) in chloride medium is negligible (<5%) though a slight increase is observed at low and high acid molarity. The extraction behaviour of palladium(II) shows a positive dependence on the acidity of sulphuric acid and the extraction increases substantially with the increasing acid molarity attaining hundred percent extraction at 4.0 mol L^{-1} H_2SO_4. This suggests that the sulphate medium favours the formation of extractable species of Pd(II). However, the extraction of Pd(II) is around 70% at 0.10 mol L^{-1} HNO_3 and decreases with increasing acidity becoming negligible around 2.0 mol L^{-1} HNO_3.

Ir(III) and Ru(III) distributes between the aqueous and organic phase creating difficulty in their selective extraction and selective stripping while Rh(III) shows low or negligible extraction in all the three acids with 0.10 mol L^{-1} Cyanex 923. Detailed studies were carried out on platinum and palladium only using 0.10 mol L^{-1} Cyanex 923 at 1.0 mol L^{-1} HCl and H_2SO_4, respectively.

Effect of equilibration time

The effect of equilibrium time (1-30 minutes) on the extraction of Pt(IV) and Pd(II) was studied using 0.1 mol L^{-1} Cyanex 923 (figure 3A.4). It was observed that under the experimental conditions a minimum of four and five minutes equilibration time was sufficient for attaining limiting extraction of Pt(IV) and Pd(II), respectively. It was checked that prolonged shaking did not affect the results. In all the subsequent studies the aqueous and the organic phase were contacted for six minutes unless mentioned otherwise.

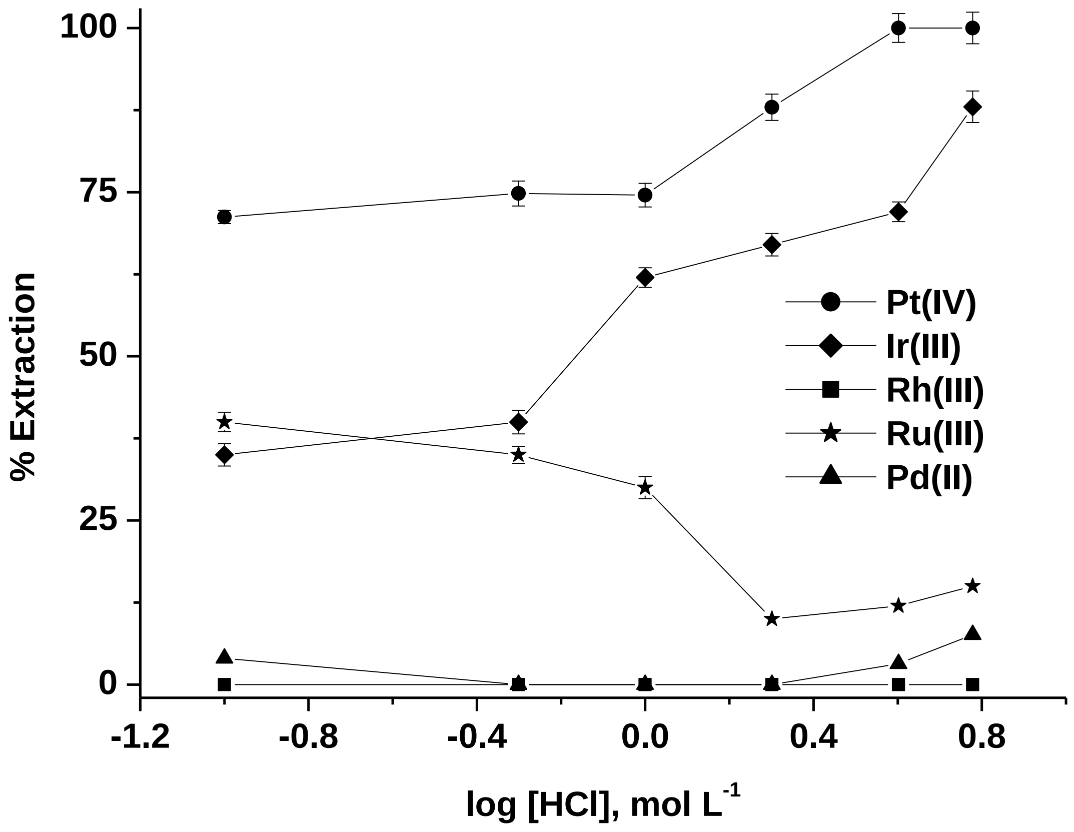


FIGURE 3A.1: Effect of concentration of hydrochloric acid on the extraction of Pt(IV), Ir(III), Rh(III), Ru(III) and Pd(II)

Conditions

[Cyanex 923] = 0.10 mol L^{-1}

[Metal ion] = 5 x 10^{-4} mol L^{-1}

[HCl] = 0.1 - 6.0 mol L^{-1}

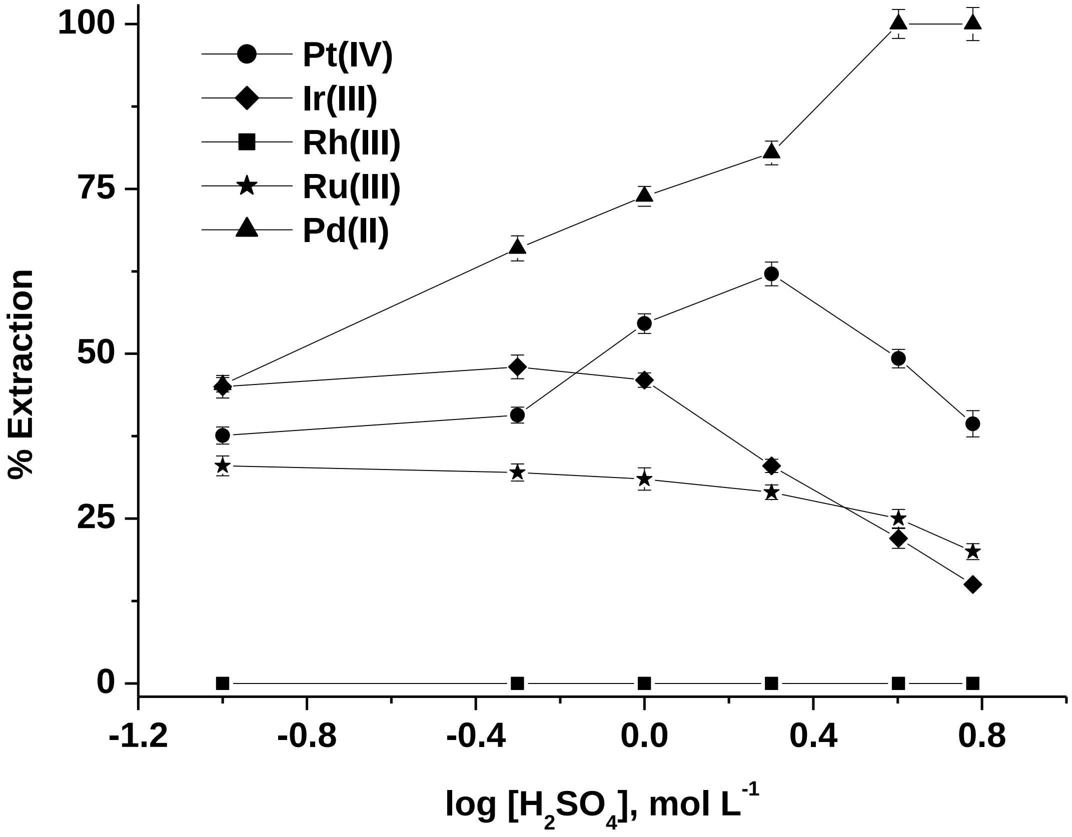


FIGURE 3A.2: Effect of concentration of sulphuric acid on the extraction of Pt(IV), Ir(III), Rh(III), Ru(III) and Pd(II)

Conditions

[Cyanex 923] = 0.10 mol L^{-1}

[Metal ion] = 5 x 10^{-4} mol L^{-1}

[H_2SO_4] = 0.1 - 6.0 mol L^{-1}

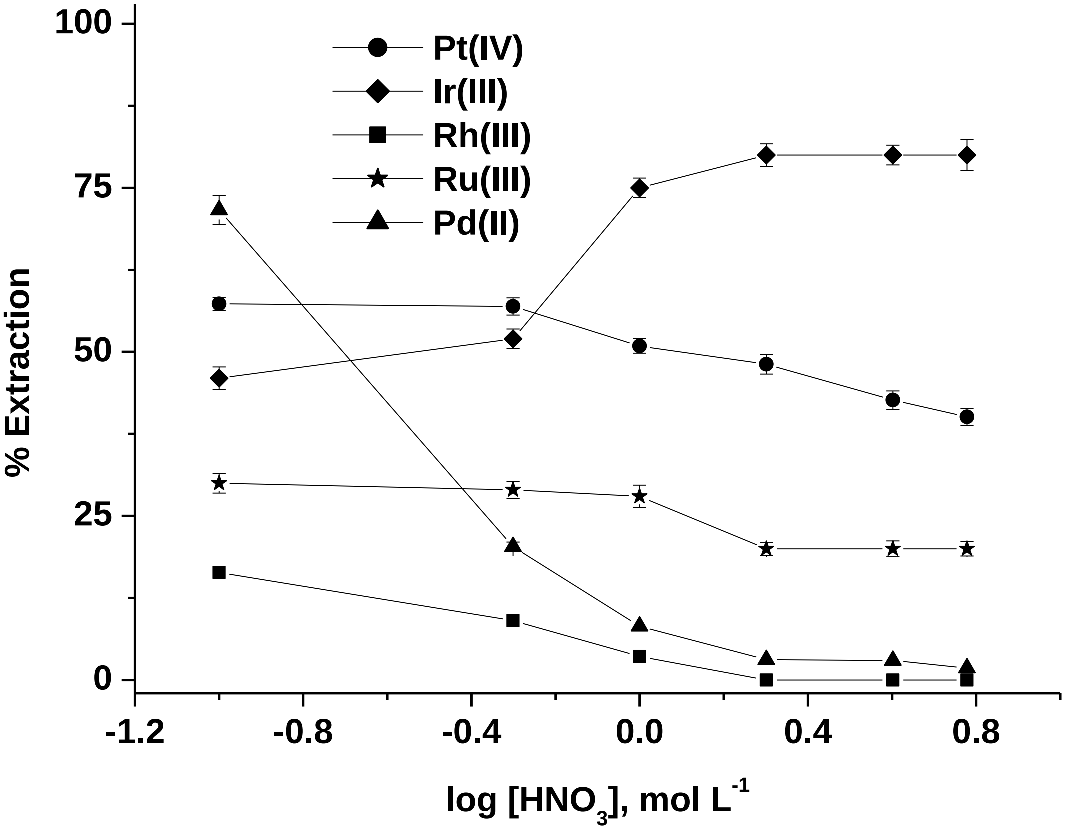


FIGURE 3A.3: Effect of concentration of nitric acid on the extraction of Pt(IV), Ir(III), Rh(III), Ru(III) and Pd(II)

Conditions

[Cyanex 923] = 0.10 mol L^{-1}
[Metal ion] = 5 x 10^{-4} mol L^{-1}
[HNO$_3$] = 0.1 - 6.0 mol L^{-1}

Effect of temperature on the extraction

The effect of temperature on the distribution of Pt(IV) and Pd(II) was investigated in the range of 10-50^{o}C. The results are illustrated in figure 3A.5 where plots between 1000/T and log K gave straight lines with positive slope values of 0.64 and 2.4 for Pt(IV) and Pd(II), respectively. In both the cases the results indicate a decrease in percent extraction with the increasing temperature thus suggesting the process to be exothermic. The values of ΔH as calculated using Van’t Hoff equation $-\ln K_{ex} = \Delta H/R.1/T$, were found to be -35.41 kJ/mol and -16.55 kJ/mol, for Pt(IV) and Pd(II), respectively.

Effect of extractant concentration

The metal to extractant ratio in the extracted platinum/palladium species was determined by varying Cyanex 923 concentration from 0.03 to 0.5 mol L^{-1} at 1.0 mol L^{-1} hydrochloric acid and sulphuric acid for Pt(IV) and Pd(II), respectively. The extraction increases with the increase in the extractant concentration. The plots drawn between log [Extractant] and log D (figure 3A.6) gave straight lines with a slope value around two for both the metal ions, thus suggesting the involvement of two molecules of the extractant in the formation of the extracting species. Similar results were obtained by Duche et al (53) for the extraction of Pd(II) from bromide medium using Cyanex 923.

Effect of the nature of diluent

To discern the effect of nature of diluents various aromatic and aliphatic diluents namely nitrobenzene, cyclohexane, chloroform, toluene, xylene, kerosene and n-hexane were employed. For both the metal ions the results (table 3A.1) indicate no correlation in the extent of extraction and the dielectric constant or chemical nature of the diluents. Pt(IV) and Pd(II) showed comparable extraction with all the diluents except chloroform in which very low extraction of palladium was observed. Toluene was preferred as a diluent for all other studies since it provides quicker phase separation.

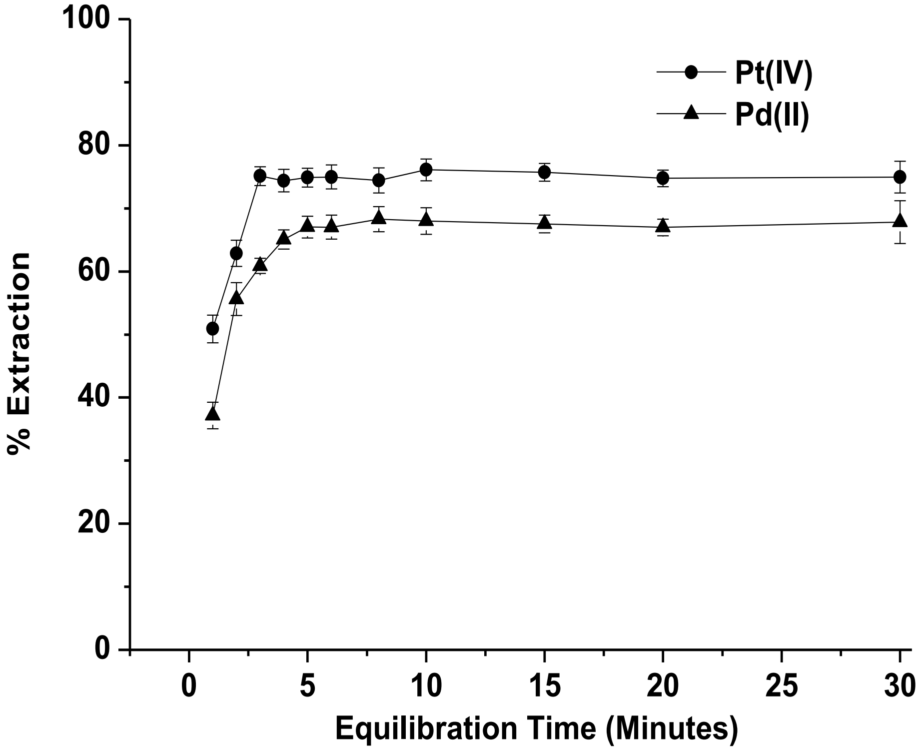


FIGURE 3A.4: Effect of equilibration time on the extraction of Pt(IV) and Pd(II)

Conditions

[Cyanex 923] = 0.10 mol L^{-1}

[Metal ion] = 5 x 10^{-4} mol L^{-1}

[HCl] = 1.0 mol L^{-1} (Pt(IV))

[H_2SO_4] = 1.0 mol L^{-1} (Pd(II))

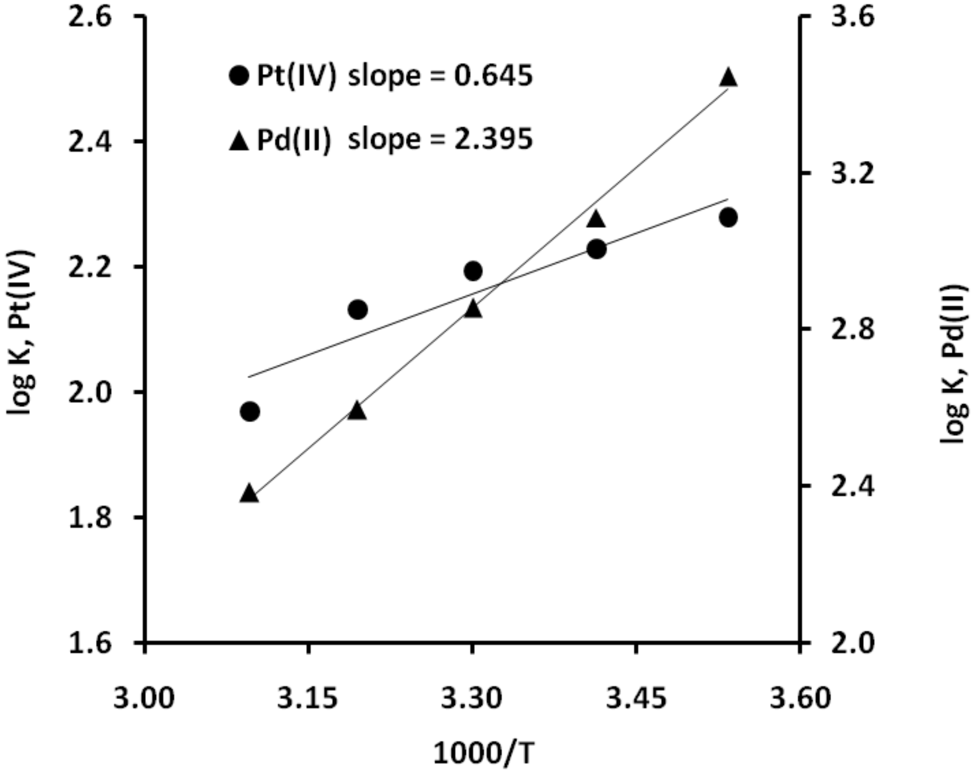


FIGURE 3A.5: Effect of temperature on the extraction of Pt(IV) and Pd(II)

Conditions

[Cyanex 923] = 0.10 mol L^{-1}
[Metal ion] = 5 x 10^{-4} mol L^{-1}
[HCl] = 1.0 mol L^{-1} (Pt(IV))
[H_2SO_4] = 1.0 mol L^{-1} (Pd(II))

Loading Capacity of Cyanex 923 towards Pt(IV) and Pd(II)

The loading capacity of Cyanex 923 in toluene (0.10 mol L^{-1}) was studied by equilibrating Pt(IV)/Pd(II) solution at 6.0 mol L^{-1} HCl/H_2SO_4 at a fixed organic to aqueous phase ratio 1:1. The two phases were separated and the metal ion concentration transferred to the organic phase was determined. The same organic phase was used again for the extraction of Pt(IV)/Pd(II) from fresh aqueous phase (figure 3A.7). This procedure was repeated till no further extraction of Pt(IV)/Pd(II) was observed in the organic phase. The maximum loading obtained is 80 mM Pt(IV) per 0.10 M extractant after ten stages and 100 mM Pd(II) per 0.10 M extractant after eight stages. Similar results were obtained for the loading of Pd(II) from nitrate medium on Cyanex 471X (56).

Hydrolytic stability and regeneration capacity of Cyanex 923

The stability and recycling capacity of an extractant needs to be evaluated to assess its utility as an extractant for commercial purposes. The aforesaid characteristics of Cyanex 923 have been investigated for Pt(IV) and Pd(II) in terms of change in percent extraction.

The hydrolytic stability of the extractant towards HCl and H_2SO_4 was checked by keeping its toluene solution in contact with 6.0 mol L^{-1} HCl/H_2SO_4 for fifty days with intermittent shaking. The extraction of Pt(IV) and Pd(II) was checked periodically after five days. An insignificant variation (±3%) in the percent extraction of Pt(IV) and Pd(II) (figure 3A.8) was observed even after a contact time of fifty days. It may be mentioned that in the present studies acid molarity beyond 6.0 mol L^{-1} has not been used. Therefore the stability

of the extractant has been checked towards 6.0 mol L^{-1} HCl/H_2SO_4. Stability of Cyanex 923 towards 5.0 mol L^{-1} H_2SO_4 and 10.0 mol L^{-1} HCl is already reported [1, 38].

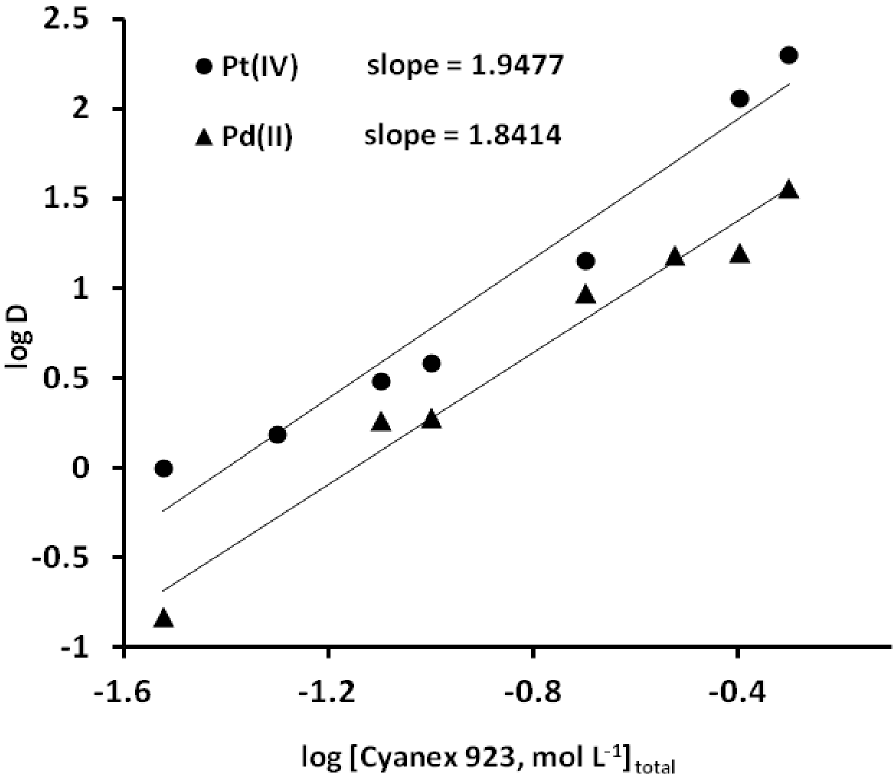


FIGURE 3A.6: Effect of extractant concentration on the extraction of Pt(IV) and Pd(II)

Conditions

[Cyanex 923] = 0.10 mol L^{-1}
[Metal ion] = 5 x 10^{-4} mol L^{-1}
[HCl] = 1.0 mol L^{-1} (Pt(IV))
[H_2SO_4] = 1.0 mol L^{-1} (Pd(II))

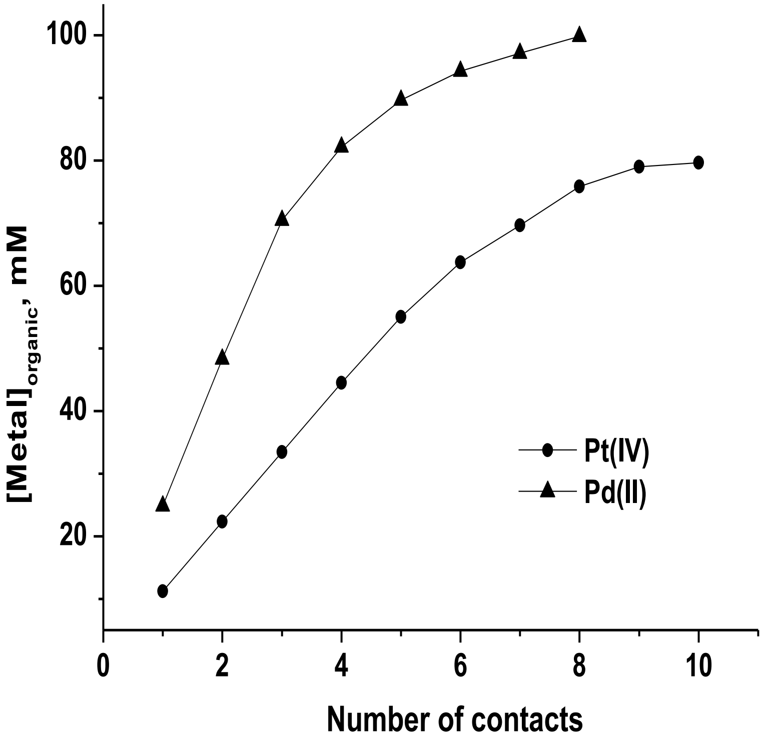


FIGURE 3A.7: Loading capacity of Cyanex 923 towards Pt(IV) and Pd(II)

Conditions

[Cyanex 923] = 0.10 mol L^{-1}
[HCl] = 1.0 mol L^{-1} (Pt(IV))
[H_2SO_4] = 1.0 mol L^{-1} (Pd(II))

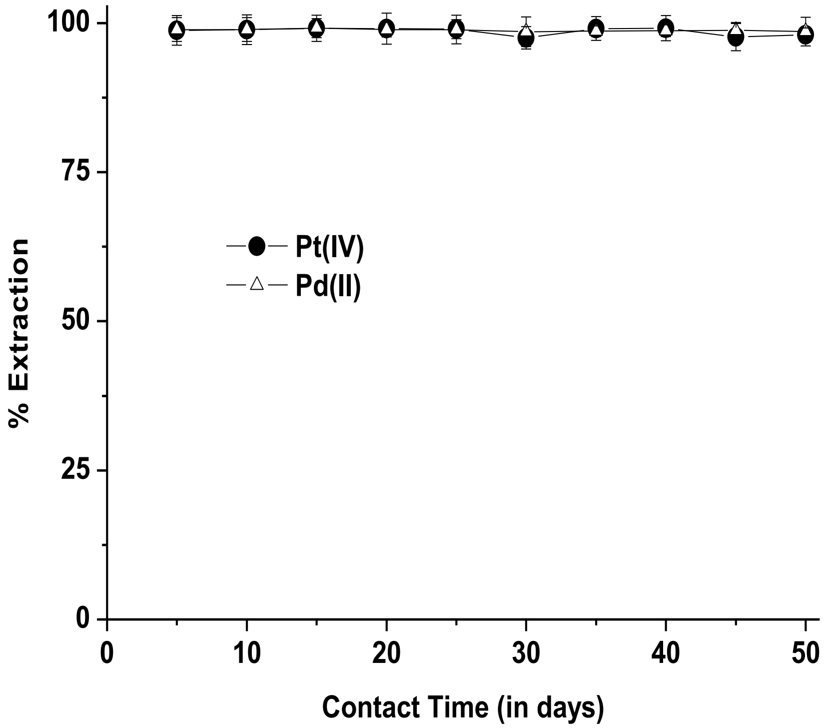


FIGURE 3A.8: Variation in the extraction of Pt(IV)/Pd(II) using Cyanex 923 solution kept in contact with 6.0 mol L^{-1} HCl/H_2SO_4

Conditions

[Cyanex 923] = 0.10 mol L^{-1}
[Metal ion] = 5 x 10^{-4} mol L^{-1}
[HCl] = 6.0 mol L^{-1} (Pt(IV))
[H_2SO_4] = 6.0 mol L^{-1} (Pd(II))

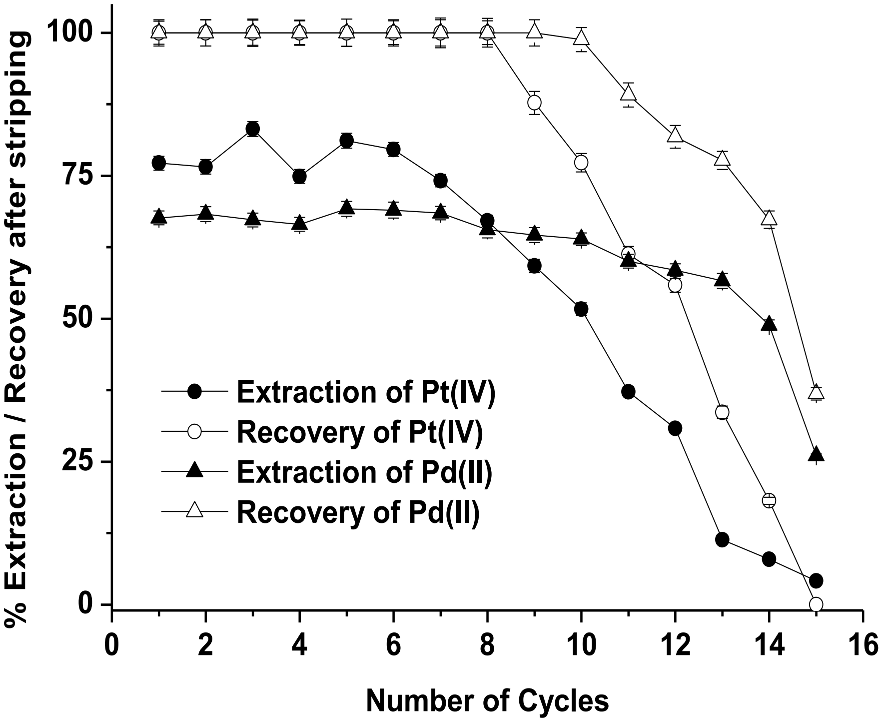


FIGURE 3A.9: Variation in the extraction / recovery of Pt(IV)/Pd(II) in successive

Conditions

[Cyanex 923] = 0.10 mol L^{-1}

[Metal ion] = 5 x 10^{-4} mol L^{-1}

[HCl] = 1.0 mol L^{-1} (Pt(IV))

[H_2SO_4] = 1.0 mol L^{-1} (Pd(II))

[Strippant] = 5.0 mol L^{-1} $HClO_4$

Table 3A.1. Effect of the nature of various diluents on the extraction of Pt(IV) and Pd(II).

Diluent	Dielectric constant	Percent extraction	
		Pt(IV)	Pd(II)
Nitrobenzene	35.70	73.40	67.46
Cyclohexane	18.3	72.8	62.42
Chloroform	4.81	73.01	8.38
Toluene	2.44	75.10	67.58
Xylene	2.20	74.29	65.89
Kerosene	2.02	73.33	64.08
n-hexane	1.891	73.03	68.01

Conditions

[Cyanex 923] = 0.10 mol L^{-1}

[Metal ion] = 5 x 10^{-4} mol L^{-1}

[HCl] = 1.0 mol L^{-1} (Pt(IV))

[H_2SO_4] = 1.0 mol L^{-1} (Pd(II))

For determining the regeneration capacity of the extractant successive extraction/stripping cycles for Pt(IV)/Pd(II) were carried out. Pt(IV)/Pd(II) was extracted using 0.10 mol L^{-1} Cyanex 923 and stripped using 5.0 mol L^{-1} $HClO_4$. The organic phase after stripping was regenerated by washing with water until the washings were nearly neutral. The recovery of the metal ion (Pt(IV)/Pd(II)) in each step was calculated from the amount of the metal extracted in the organic phase in that particular cycle. Results revealed practically insignificant change (±3%) in the percent extraction/recovery of Pt(IV) and Pd(II) up to seven and eleven cycles, respectively (figure 3A.9).

Stripping reagents

Various stripping reagents were tried for the stripping of Pt(IV), Rh(III) and Pd(II) from the loaded Cyanex 923. The results indicating the efficiency of the different stripping reagents are given in table 3A.2. Solutions of $HClO_4$ (5.0 mol L^{-1}), H_2SO_4 (5.0 mol L^{-1}) and malonic acid (0.40 mol L^{-1}) were found effective for the quantitative stripping of Pt(IV) whereas, $HClO_4$ (5.0 mol L^{-1}) and acidic solution of 1% sodium salt of dimethyl glyoxime were effective for Pd(II). For all further studies 5.0 mol L^{-1} $HClO_4$ was used for the recovery of Pt(IV) and Pd(II) from the loaded organic phase. If both the metal ions are present simultaneously then Pt(IV) was stripped first using 5.0 mol L^{-1} H_2SO_4 followed by the stripping of Pd(II) with 5.0 mol L^{-1} $HClO_4$. In the case of Rh(III) quantitative stripping was achieved with 5.0 mol L^{-1} HCl.

Extraction behaviour of associated metal ions

The extraction behavior of associated metal ions is investigated only from HCl, H_2SO_4 and HNO_3.

HCl

The extraction behaviour of associated metal ions, namely Au(III), Fe(III), Cr(III), Al(III), Cu(II), Ni(II), Co(II) and Fe(II) from HCl (0.10 to 6.0 mol L^{-1}) medium is shown in figure 3A.10. The extraction of associated metal ions is poor (<10%) except Au(III) and Fe(III). Au(III) is extracted quantitatively whereas Fe(III) is extracted between 25 and 35% in the investigated range of acid molarity. Extraction behavior of Ag(I) was not investigated from HCl medium, as there are chances of precipitation of silver in chloride medium.

H_2SO_4

The extraction behaviour of different associated metal ions from sulphuric acid (0.10 to 6.0 mol L^{-1}) medium is shown in figure 3A.11. As depicted in figure the extraction of Cr(III), Al(III), Cu(II), Ni(II), Co(II) and Fe(II) is poor (<10%) in the studied range of acid molarity. Au(III) is extracted quantitatively while Fe(III) shows percent extraction between 10 and 25. Ag(I) shows a maximum extraction of ~33% at 0.50 mol L^{-1} H_2SO_4.

HNO_3

The extraction behaviour of different associated metal ions from nitric acid (0.10 to 6.0 mol L^{-1}) medium is shown in figure 3A.12. The distribution of Cr(III), Al(III), Cu(II), Ni(II) and Fe(II) from HNO_3 medium is negligible where as Au(III) and Ag(I) shows quantitative extraction. The percent extraction of Fe(III) decreases with increasing molarity of HNO_3 and beyond 2.0 mol L^{-1} HNO_3 a slight increase is observed.

Separations

The partition data obtained for the metal ions provide conditions for the separation of Pt(IV), Rh(III) and Pd(II) from each other and from the associated metal ions either by selective extraction or selective stripping. The results indicating the conditions for the separations and the percentage recovery of the metal ions are tabulated in tables 3A.3 and 3A.4.

Binary separations

Pt(IV)

The extraction behaviour of Pt(IV) from HCl medium is quite different from most of the associated metal ions, therefore the separation of Pt(IV) from other associated

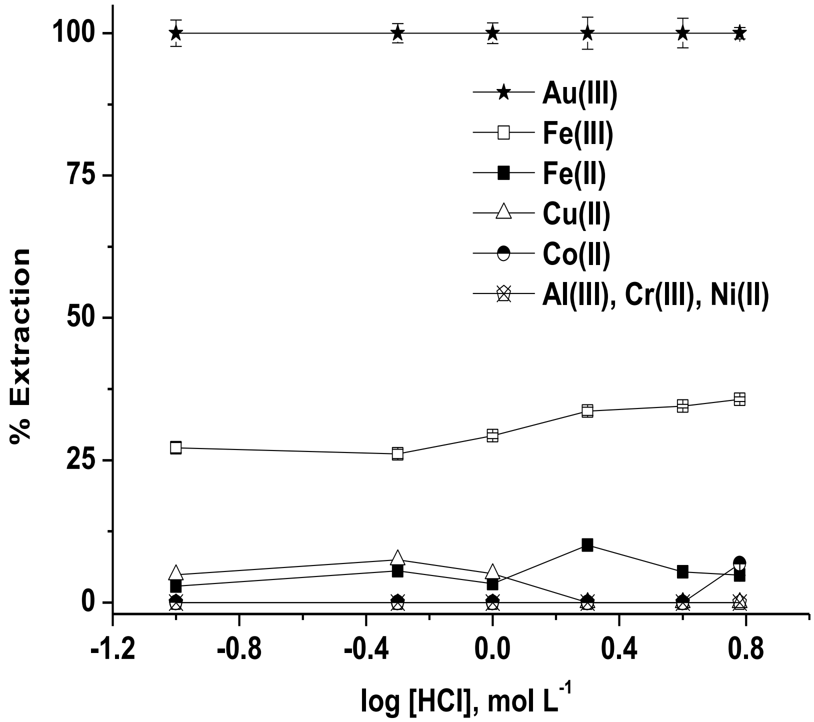


FIGURE 3A.10: Effect of concentration of hydrochloric acid on the extraction of associated metal ions

Conditions

[Cyanex 923] = 0.10 mol L^{-1}

[Metal ion] = 5 x 10^{-4} mol L^{-1}

[HCl] = 0.1 - 6.0 mol L^{-1}

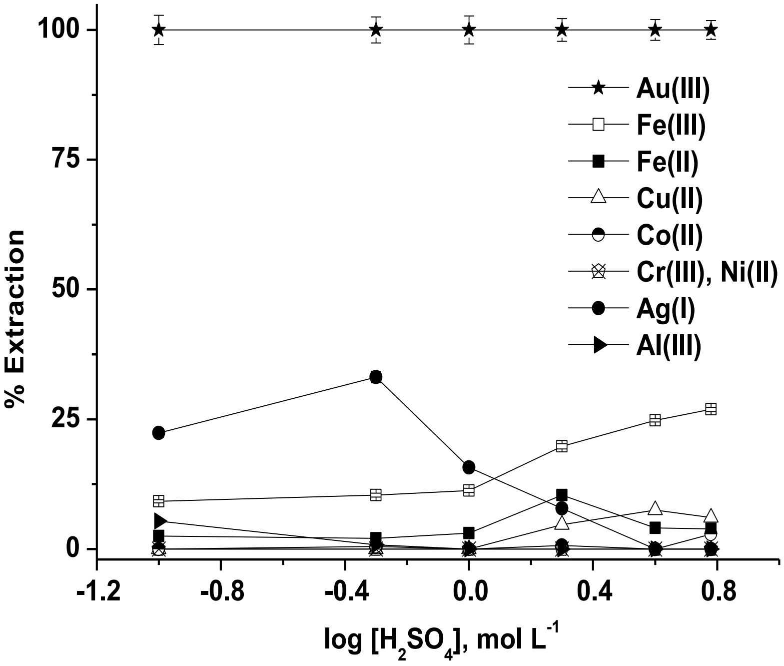


FIGURE 3A.11: Effect of concentration of sulphuric acid on the extraction of associated metal ions

Conditions

[Cyanex 923] = 0.10 mol L^{-1}

[Metal ion] = 5 x 10^{-4} mol L^{-1}

[H_2SO_4] = 0.1 - 6.0 mol L^{-1}

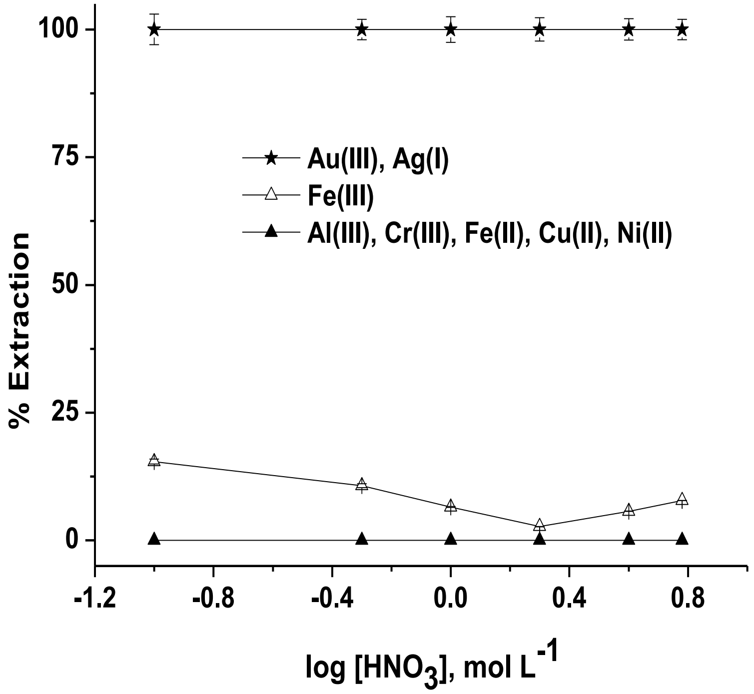


FIGURE 3A.12: Effect of concentration of nitric acid on the extraction of associated metal ions

Conditions

[Cyanex 923] = 0.10 mol L^{-1}
[Metal ion] = 5 x 10^{-4} mol L^{-1}
[HNO$_3$] = 0.1 - 6.0 mol L^{-1}

Table 3A.2. Efficiency of various stripping reagents for Pt(IV) and Pd(II).

Strippants used	% Stripping		
	Pt(IV)	Pd(II)	Rh(III)
5 mol L^{-1} $HClO_4$	100	100	92.0
0.1 mol L^{-1} EDTA	16.46	30.0	-
5 mol L^{-1} H_2SO_4	85.26	0	100
1% DMG-Na +3 M HCl + 2 mol L^{-1} HNO_3	30.1	100	-
0.4 mol L^{-1} Malonic acid	99.84	82.47	45.0
0.1 mol L^{-1} Thiourea + 0.1 mol L^{-1} HNO_3	26.83	50.5	-
0.1 mol L^{-1} Thiourea + 1 mol L^{-1} $HClO_4$	36.96	63.52	-
0.1 mol L^{-1} Thiourea + 0.2 mol L^{-1} HCl	27.01	32.13	-
1.0 mol L^{-1} HCl	-	-	63.2
5.0 mol L^{-1} HCl	12.84	79.31	100

Conditions

[Cyanex 923] = 0.10 mol L^{-1}

[Metal ion] = 5 x 10^{-4} mol L^{-1}

metal ions was carried out from HCl medium. Pt(IV) is selectively extracted from an aqueous solution containing Rh(III)/Cr(III)/Al(III)/Cu(II)/Ni(II)/Co(II)/Fe(II) at 5.0 mol L^{-1} HCl using 0.1 mol L^{-1} Cyanex 923. Fe(III) is partially co-extracted with Pt(IV) at 5.0 mol L^{-1} HCl therefore for Pt(IV)-Fe(III) separation, Fe(III) was first reduced to Fe(II) using 0.05 mol L^{-1} ascorbic acid followed by the extraction of Pt(IV) at 5.0 mol L^{-1} HCl leaving Fe(II) in the aqueous phase. Pt(IV) was then recovered by washing the organic phase with 5.0 mol L^{-1} $HClO_4$. For Pt(IV)-Au(III) separation, the two are quantitatively extracted at 5.0 mol L^{-1} HCl. Au(III) was scrubbed from the organic phase using water followed by the stripping of Pt(IV) employing 5.0 mol L^{-1} $HClO_4$. Pt(IV)-Pd(II) separation was carried out at 2.0 mol L^{-1} HCl as Pt(IV) is extracted leaving Pd(II) in the aqueous phase.

Pd(II)

The separation of Pd(II) from the associated metal ions has been achieved at 5.0 mol L^{-1} H_2SO_4. At this acidity Pd(II) is extracted quantitatively leaving Rh(III)/Cr(III)/Al(III)/Cu(II)/Ni(II)/Co(II)/Fe(II)/Ag(I) in the aqueous phase. Pd(II) was scrubbed from the organic phase using 5.0 mol L^{-1} $HClO_4$. Here again Fe(III) was reduced to Fe(II) prior to separation. At 5.0 mol L^{-1} H_2SO_4 Pd(II) is quantitatively extracted along with ~30% Pt(IV). Thus for the separation of Pd(II) from Pt(IV), the co-extracted Pt(IV) was scrubbed by equilibrating the loaded organic phase thrice with 5.0 mol L^{-1} H_2SO_4 followed by the recovery of Pd(II) with 5.0 mol L^{-1} $HClO_4$. Both Au(III) and Pd(II) are quantitatively extracted at 5.0 mol L^{-1} H_2SO_4 and the two were separated by selectively stripping Au(III) with water followed by stripping of Pd(II) with 5.0 mol L^{-1} $HClO_4$.

Rh(III)

Rhodium coated alumina catalyst is widely used in various industries for hydrogenation reactions. Therefore recovery of rhodium from spent rhodium coated alumina catalyst assumes great significance. In order to explore the possibility of separation of Rh(III) and Al(III) the extraction behavior of the two metal ions was further investigated from nitrate with 2.0 mol L^{-1} Cyanex 923 observing an equilibration time of one and six minutes as shown in figure 3A.13. When the equilibration time of one minute was observed Rh(III) showed 35% extraction at 0.10 mol L^{-1} HNO_3 followed by a continuous decrease. With an equilibration time of six minutes

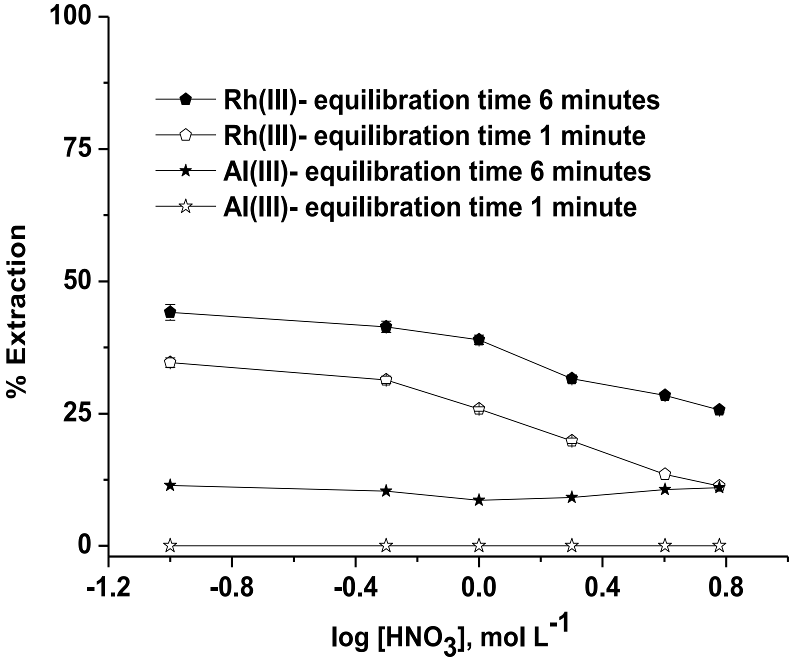


FIGURE 3A.13: Effect of concentration of nitric acid on the extraction of Rh(III) and Al(III)

Conditions

[Cyanex 923] = 2.0 mol L^{-1}
[Metal ion] = 5 x 10^{-4} mol L^{-1}
[HNO$_3$] = 0.1 - 6.0 mol L^{-1}

Table 3A.3. Some binary separations of Pt(IV) from associated metal ions in hydrochloric acid medium using 0.10 mol L^{-1} Cyanex 923

Metal ions separated	Molar ratio	Acid molarity (mol L^{-1})	Metal ion remained in the aqueous phase (%)	Metal ion transferred into the organic phase (%)	Metal ion stripped* from the organic phase (%)[a]	Separation Factor, β
Pt(IV):Rh(III)	1:10	5	100 ±0.2, Rh	99 ± 1.2, Pt	99 ± 1.1, Pt	3.9 x 10^5
	10:1		100 ±0.3, Rh	98 ± 1.1, Pt	99 ± 0.7, Pt	2.0 x 10^5
Pt(IV):Au(III)	1:10	5	- -	99 ± 1.2, Pt 100 ± 1.1, Au	99 ± 1.3, Pt 100 ± 1.1, Au	
	10:1		- -	99 ± 1.0, Pt 100 ± 1.0, Au	98 ± 1.0, Pt 99 ± 1.0, Au	
Pt(IV):Cr(III)	1:10	5	99 ± 1.3, Cr	97 ± 1.3, Pt	98 ± 1.1, Pt	1.0 x 10^4
	10:1		99 ± 1.0, Cr	96 ± 1.5, Pt	99 ± 1.2, Pt	9.7 x 10^3
Pt(IV):Cu(II)	1:10	5	99 ± 1.0, Cu	99 ± 0.8, Pt	100 ± 1.0, Pt	3.2 x 10^4
	10:1		100 ± 1.0, Cu	99 ± 0.8, Pt	100 ± 0.9, Pt	5.3 x 10^4
Pt(IV):Ni(II)	1:10	5	99 ± 1.1, Ni	97 ± 1.1, Pt	98 ± 0.8, Pt	1.1 x 10^4
	10:1		98 ± 1.1, Ni	98 ± 1.1, Pt	100 ± 0.8, Pt	9.1 x 10^3
Pt(IV):Co(II)	1:10	5	98 ± 1.2, Co	98 ± 1.1, Pt	97 ± 0.8, Pt	3.8 x 10^4
	10:1		99 ± 1.1, Co	98 ± 1.2, Pt	98 ± 0.8, Pt	2.7 x 10^4
Pt(IV):Pd(II) (twice extraction)	1:10	2	100 ± 1.0, Pd	99 ± 0.9, Pt	99 ± 0.7, Pt	5.1 x 10^4
	10:1		99 ± 1.2, Pd	97 ± 0.9, Pt	98 ± 0.8, Pt	8.8 x 10^4

Note: '±' refers to the standard deviation

[a] Pt(IV) stripped using 5.0 mol L^{-1} $HClO_4$ and Au(III) stripped using water.

Table 3A.4. Some Binary separations of Pd(II) from associated metal ions in sulphuric acid medium using 0.10 mol L^{-1} Cyanex 923

Metal ions separated	Molar ratio	Acid molarity (mol L^{-1})	Metal ion remained in the aqueous phase (%)	Metal ion transferred into the organic phase (%)	Metal ion stripped* from the organic phase (%)[a]	Separation factor, β
Pd(II):Pt(IV)	1:10	5	-	100 ± 0.2, Pd	99 ± 0.5, Pd	7.5 x 10^2
			69 ± 1.0, Pt	31 ± 0.8, Pt	100 ± 0.1, Pt	
	10:1		-	99 ± 0.5, Pd	98 ± 0.7, Pd	3.0 x 10^2
			73 ± 1.0 Pt	27 ± 0.9, Pt	97 ± 0.6, Pt	
Pd(II):Rh(III)	1:10	5	100 ± 0.1, Rh	98 ± 0.9, Pd	98 ± 0.9, Pd	1.9 x 10^5
	10:1		100 ± 0.2, Rh	98 ± 0.8, Pd	98 ± 0.8, Pd	1.3 x 10^5
Pd(II):Au(III)	1:10	5	-	99 ± 1.0, Pd	98 ± 0.9, Pd	
			-	98 ± 1.0, Au	99 ± 0.8, Au	
	10:1		-	97 ± 0.9, Pd	100 ± 0.9, Pd	
			-	100 ± 1.0, Au	100 ± 0.7, Au	
Pd(II):Cr(III)	1:10	5	99 ± 1.0, Cr	97 ± 1.1, Pd	98 ± 0.9, Pd	3.0 x 10^4
	10:1		100 ± 1.0, Cr	96 ± 1.2, Pd	97 ± 1.0, Pd	5.8 x 10^4
Pd(II):Al(III)	1:10	5	100 ± 0.9, Al	98 ± 0.8, Pd	98 ± 0.9, Pd	1.1 x 10^4
	10:1		99 ± 0.7, Al	99 ± 1.0, Pd	99 ± 1.0, Pd	9.4 x 10^3
Pd(II):Cu(II)	1:10	5	99 ± 1.0, Cu	99 ± 0.8, Pd	100 ± 1.0, Pd	3.1 x 10^4
	10:1		99 ± 1.0, Cu	98 ± 0.7, Pd	96 ± 1.1, Pd	4.8 x 10^4
Pd(II):Ni(II)	1:10	5	99 ± 0.9, Ni	97 ± 1.1, Pd	98 ± 0.9, Pd	1.3 x 10^4
	10:1		99 ± 0.8, Ni	97 ± 1.0, Pd	97 ± 1.0, Pd	1.2 x 10^4
Pd(II):Co(II)	1:10	5	98 ± 0.8, Co	100 ± 0.9, Pd	97 ± 1.1, Pd	4.2 x 10^4
	10:1		97 ± 1.1, Co	98 ± 0.7, Pd	98 ± 0.8, Pd	3.4 x 10^4
Pd(II):Fe(II)	1:10	5	99 ± 1.0, Cu	99 ± 0.8, Pd	100 ± 1.0, Pd	3.2 x 10^4
	10:1		98 ± 1.2, Cu	98 ± 0.7, Pd	97 ± 1.1, Pd	4.7 x 10^4
Pd(II):Ag(I)	1:10	5	97 ± 0.8, Ag	99 ± 1.0, Pd	98 ± 0.8, Pd	5.7 x 10^4
	10:1		98 ± 0.8, Ag	97 ± 1.1, Pd	98 ± 0.7, Pd	5.5 x 10^4

Note: '±' refers to the standard deviation

[a] Pd(II) stripped using 5.0 mol L^{-1} $HClO_4$, Pt(IV) stripped using 5.0 mol L^{-1} H_2SO_4 and Au(III)stripped using water.

Rh(III) shows maximum extraction of 45% at 0.10 mol L^{-1} HNO_3 which decreases thereafter exhibiting a minimum value of ~25% at 6.0 mol L^{-1} HNO_3. Al(III) is poorly extracted (8 – 12%) with 2.0 mol L^{-1} Cyanex 923 with six

minutes shaking time whereas negligibly extracted with an equilibration time of one minute. These results indicate that if desired around ninety percent Rh(III) will be extracted in four extractions at 0.10 mol L^{-1} HNO_3 using 2.0 mol L^{-1} Cyanex 923 observing an equilibration time of six minutes.

The Rh(III)-Al(III) separation was attained at 0.10 mol L^{-1} HNO_3, by equilibrating the aqueous phase four times with 2.0 mol L^{-1} Cyanex 923 for one minute only. Under these conditions around 85% of Rh(III) was extracted leaving Al(III) in the aqueous layer. Rh(III) was recovered by equilibrating the organic phase with 5.0 mol L^{-1} HCl. The separation of Rh(III) from Au(III) and Ag(I) was achieved at 4.0 mol L^{-1} HNO_3 using 0.10 mol L^{-1} Cyanex 923. At this acidity Au(III) and Ag(I) are extracted quantitatively while Rh(III) remains unextracted.

A majority of the separations planned and achieved involve those elements which are likely to be encountered in different matrices containing PGMs. Most of these separations are attained by controlling the acidity of the aqueous phase or extractant concentration. In some cases selective stripping from the organic phase proved useful. In most of the cases the stripping reagents used are simple in composition and thus further processing of the recovered metal ion may be easier. The results of binary separations proved very handy in devising systematic schemes for the recovery of Pt(IV)/Pd(II) from different matrices.

Recovery of PGMs

Recovery from synthetic mixture

Based on the extraction data a scheme (flowsheet 3A.1) was designed to separate platinum, palladium, rhodium, gold and aluminum from synthetic mixture. Using the proposed scheme the aforesaid precious metals were recovered with ~99% purity. Different steps of the scheme are detailed below.

50 mL of an aqueous solution [A1] containing equimolar concentration of Pt(IV), Rh(III), Au(III), Al(III) and Pd(II) at 5.0 mol L^{-1} H_2SO_4 was equilibrated with equal volume of 0.10 mol L^{-1} Cyanex 923. Au(III) and Pd(II) were quantitatively extracted along with a portion of Pt(IV) (~20%) while Rh(III) and major part of Pt(IV) remained in the aqueous phase [A5]. The organic phase containing Au(III), Pd(II) and a part of Pt(IV) was scrubbed with water to recover Au(III) [A2] and the co-extracted Pt(IV) was stripped thrice with equal volume of 5.0 mol L^{-1} H_2SO_4 [A3]. Finally Pd(II) was recovered using 5.0 mol L^{-1} $HClO_4$ [A4]. The raffinate [A5] was evaporated to near dryness. The residue was mixed with 10 mL of HNO_3 (2 mol L^{-1}) and again evaporated to near dryness. The procedure was repeated thrice. The residue was dissolved in 5.0 mol L^{-1} HCl adjusting the final volume to 50 mL. The resulting solution was then equilibrated with equal volume of 0.10 mol L^{-1} Cyanex 923 which extracted Pt(IV) leaving Rh(III) and Al(III) in the aqueous phase [A6]. The extracted Pt(IV) was then recovered with 5.0 mol L^{-1} $HClO_4$ [A7]. The aqueous phase [A6] was evaporated to near dryness. The residue was mixed with 10 mL of HNO_3 (2 mol L^{-1}) and again evaporated to near dryness. The procedure was repeated thrice. The residue was dissolved in 0.1 mol L^{-1} HNO_3 adjusting the final volume to 50 mL. The resulting solution was contacted four times with 2.0 mol L^{-1} Cyanex 923 observing one min shaking time. Almost 85% Rh(III) was extracted leaving Al(III) in the aqueous phase [A8]. Rh(III) was stripped using 5.0 mol L^{-1} HCl [A9]. The different organic phases were regenerated by subsequently washing them with water until the washings were almost neutral. The concentrations of the metal ions in the initial and the final solutions are given in table 3A.5.

The flow sheet has been used to recover platinum, palladium and rhodium from real samples. Different steps of the separation scheme have been omitted according to the composition of the matrix.

Validation of the developed method

The developed scheme was applied to a catalyst standard (NIST SRM-2556) for the separation and recovery of Pt(IV), Rh(III) and Pd(II). The digested solution [S1] of procured catalyst standard containing platinum(IV), rhodium(III) and palladium(II) was subjected to the proposed separation scheme (flowsheet 3A.1). As the catalyst does not contain Au(III) and Al(III) the steps corresponding to their separation have been omitted. Composition of the recovered solutions at different steps is given in table 3A.6. Recovered solutions S1, S3, S4, S6 and S7 correspond to A1, A3, A4, A6 and A7 of the proposed separation scheme.

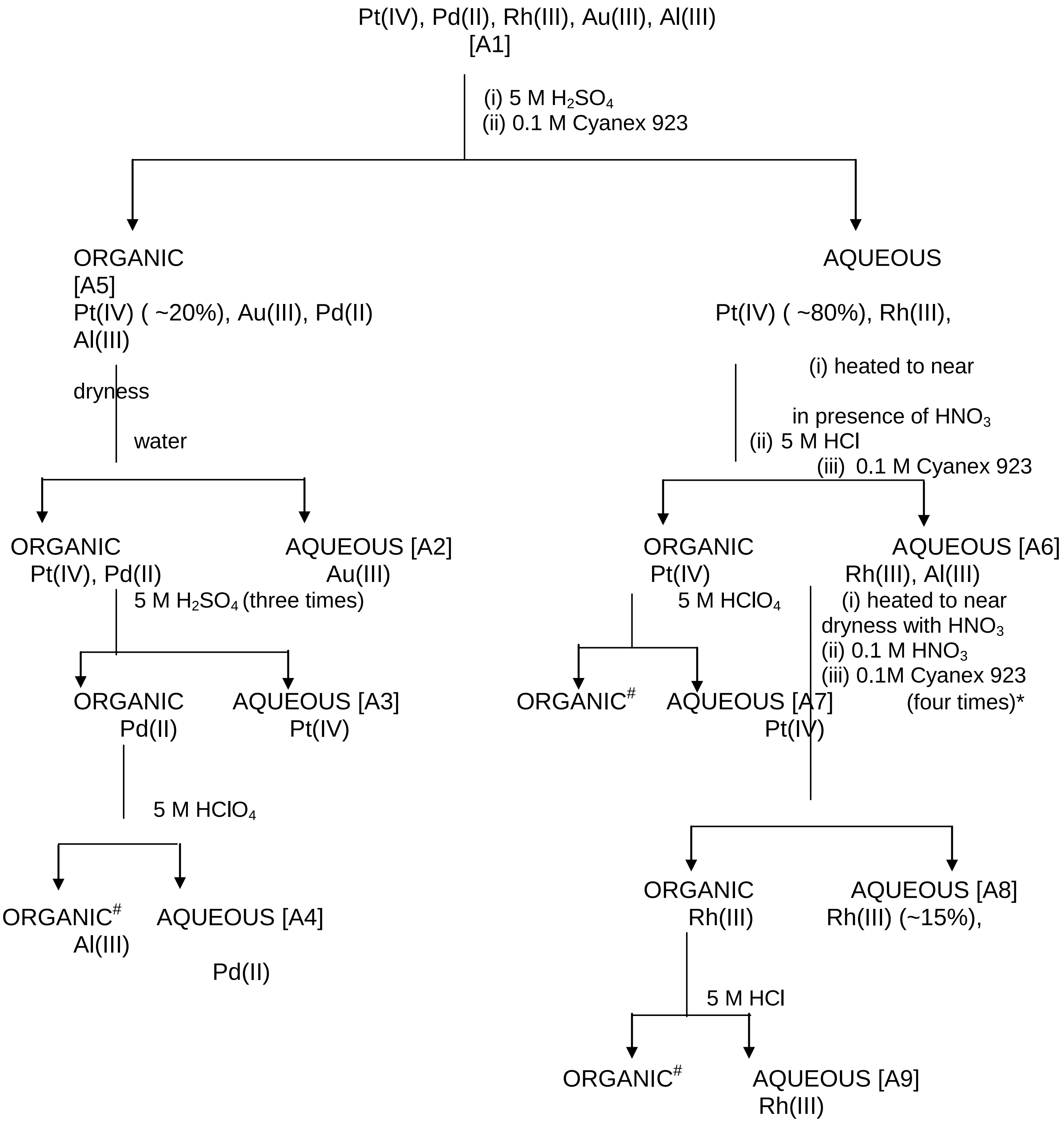
Recovery of platinum and rhodium from Pt-Rh thermocouple wire

The digested solution of the thermocouple wire, was marked as [T1] and used for the recovery of platinum and rhodium. Flowsheet 3A.2 was followed for the recovery of Pt(IV) and Rh(III) from thermocouple wire. The solution [T1] was then contacted with equal volume of 0.10 mol L^{-1} Cyanex 923 in toluene. Pt(IV) was quantitatively extracted while Rh(III) remained in the aqueous phase [T2]. The extracted Pt(IV) was stripped using 5.0 mol L^{-1} $HClO_4$ [T3]. The concentration of the metal ions in [T1], [T2] and [T3] solution is given in table 3A.7.

Recovery of palladium and rhodium from coated ceramic honeycomb

The gifted coated ceramic honeycomb containing Pd and Rh was used for the recovery of palladium. The digested solution was marked as [H1] and used for the recovery of palladium and rhodium (flowsheet 3A.3). The solution was then equilibrated with equal volume of 0.10 mol L^{-1} Cyanex 923. Pd(II) was quantitatively extracted leaving Rh(III) in the aqueous phase [H2]. The extracted Pd(II) was recovered using 5.0 mol L^{-1} $HClO_4$ [H3]. table 3A.8 gives the composition of initial and final solutions.

Flowsheet 3A.1: Recovery of PGMs from synthetic mixture using Cyanex 923



* equilibration time was 1 min, and for rest of the steps equilibration time was 6 min.

\# organic phase can be regenerated by washing with water.

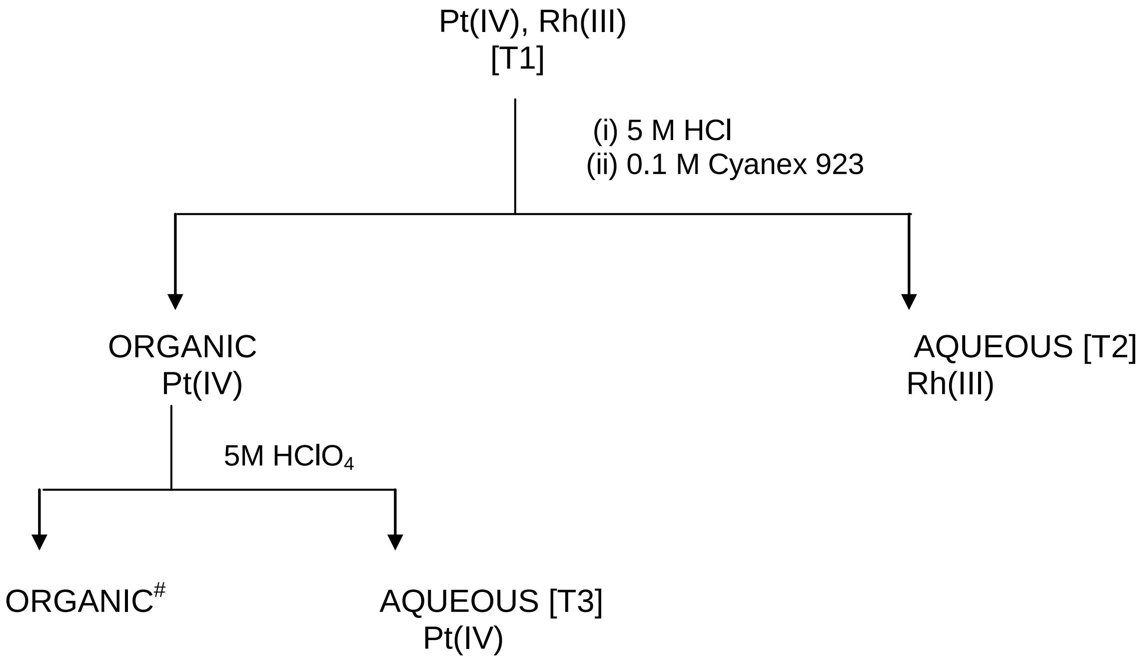
Recovery of palladium from spent palladium coated alumina catalyst

The leached solution of spent catalyst was marked as [C_1] and used for the recovery of palladium following the flowsheet 3A.4. It was checked that keeping the powdered spent catalyst sample in contact with H_2SO_4 for ten days did not enhance the amount of palladium leached out. The solution was then contacted with equal volume of 0.10 mol L^{-1} Cyanex 923. Pd(II) was quantitatively extracted while Al(III) remained in the aqueous phase [C_2]. The extracted Pd(II) was recovered using 5.0 mol L^{-1} $HClO_4$ [C_3]. The composition of [C_1], [C_2] and [C_3] solutions are given in table 3A.9.

The data embodied in the present chapter highlight the potential of Cyanex 923 for the separation and recovery of Pt(IV), Rh(III) and Pd(II). Quantitative extraction of Pt(IV) and Pd(II) is achieved from HCl and H_2SO_4 media, respectively using 0.1 mol L^{-1} Cyanex 923 whereas around 50% Rh(III) is extracted with 2.0 mol L^{-1} Cyanex 923 from 0.10 mol L^{-1} HNO_3. If desired quantitative extraction of Rh(III) can be achieved by multiple extractions with 2.0 mol L^{-1} Cyanex 923. The distribution patterns of associated metal ions are such that a majority of separations involving Pt(IV) or Pd(II) and associated metal ions are attained by controlling the acidity of the aqueous phase. In some of the cases, selective stripping has proved to be useful for the separations. The strippants used for the said purpose are invariably simple in composition and they may not present problem in further processing of the recovered metal ions. The conditions developed for the binary separations offer background data for developing the schemes to recover Pt(IV)/Pd(II) and other metal ions from complex matrices. The recovered metal solutions are around 95-99 % pure. The author has chosen some selected matrices for the recovery of Pt(IV)/Rh(III)/Pd(II) and the data can be used for the processing of other Pt(IV)/Rh(III)/Pd(II) bearing matrices.

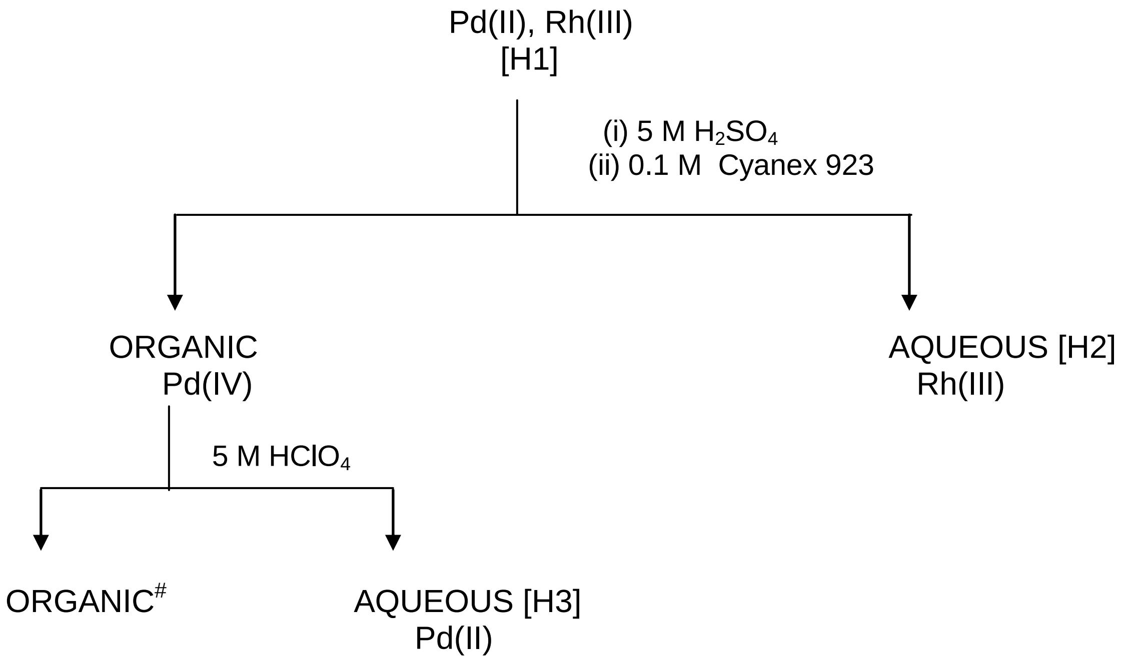
The data presented in this chapter is in press for publication in the journal “Hydrometallugy”.

Flowsheet 3A.2: Recovery of Pt(IV) and Rh(III) from thermocouple wire using Cyanex 923



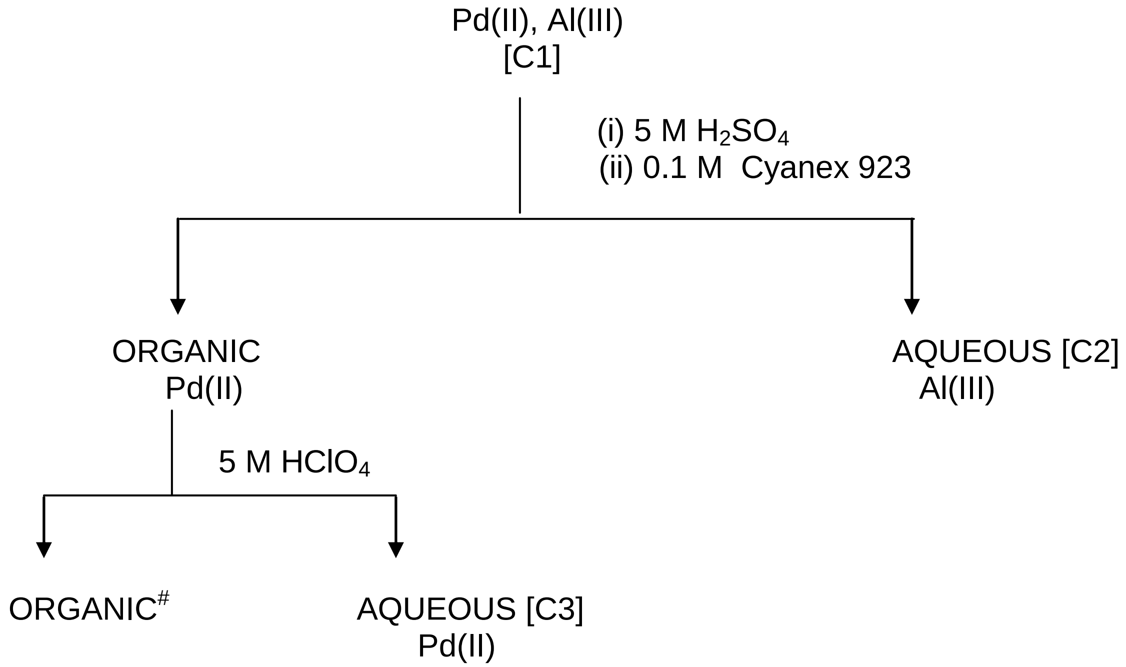
organic phase can be regenerated by washing with water.

Flowsheet 3A.3: Recovery of Pd(IV) and Rh(III) from coated ceramic honeycomb using Cyanex 923



organic phase can be regenerated by washing with water.

Flowsheet 3A.4: Recovery of Pd(II) from palladium coated alumina catalyst using Cyanex 923



organic phase can be regenerated by washing with water.

Table 3A.5. Recovery of Pt(IV), Pd(II), Rh(III), Au(III) and Al(III) from a synthetic mixture using 0.10 mol L^{-1} Cyanex 923

Metal ions	Composition of solution [A1] (mg/l)	Composition of solution [A2] (mg/l)	Composition of solution [A3] (mg/l)	Composition of solution [A4] (mg/l)	Composition of solution [A7] (mg/l)	Composition of solution [A8] (mg/l)	Composition of solution [A9] (mg/l)	Recove (%)
Pt	101.3 ± 2.0	<0.05	20.4 ± 1.2	<0.05	79.8 ± 2.0	<0.05	<0.05	98.9
Pd	52.9 ± 1.8	<0.05	<0.05	51.7 ± 1.6	<0.05	<0.05	<0.05	97.73
Rh	50.1 ± 2.0	<0.1	<0.1	<0.1	<0.1	6.7 ± 0.5	44.5 ± 1.4	99.7
Au	95.2 ± 1.9	94.8 ± 1.8	<0.05	<0.05	<0.05	<0.05	<0.05	99.6
Al	135.2 ± 2.1	<0.1	<0.1	<0.1	<0.1	135.3 ± 1.9	<0.1	100

Note: '±' refers to the standard deviation

<0.05/<0.1 refers to less than the detection limit of the corresponding metal ion.

Table 3A.6. Recovery of Pt(IV), Rh(III) and Pd(II) from catalyst standard (NIST SRM-2556) using 0.10 mol L^{-1} Cyanex 923

Metal ions	Composition of solution [S1] (mg/l)	Composition of solution [S3] (mg/l)	Composition of solution [S4] (mg/l)	Composition of solution [S5] (mg/l)	Composition of solution [S6] (mg/l)	Composition of solution [S7] (mg/l)	Recovery (%)	Purity (%)
Pt	13.04 ± 0.4	2.74 ± 0.1	<0.05	10.22 ± 0.3	<0.05	10.17 ± 0.2	99.0	
Pd	27.66 ± 0.7	<0.05	27.54 ± 0.5	<0.05	<0.05	<0.05	99.56	
Rh	2.05 ± 0.06	<0.1	<0.1	2.07 ± 0.05	2.03 ± 0.08	<0.1	99.02	

Note: '±' refers to the standard deviation

<0.05/<0.1 refers to less than the detection limit of the corresponding metal ion.

Table 3A.7. Recovery of Pt(IV) and Rh(III) from thermocouple wire using Cyanex 923

Metal ions	Composition of solution [T1] (mg/l)	Composition of solution [T2] (mg/l)	Composition of solution [T3] (mg/l)	Recovery (%)	Purity (%)
Pt	6.6 ± 0.5	<0.05	6.8 ± 0.6	100	98.55
Rh	2.2 ± 0.2	2.3 ± 0.2	<0.1	100	97.87

Note: '±' refers to the standard deviation

<0.05/<0.1 refers to less than the detection limit of the corresponding metal ion.

Table 3A.8. Recovery of Pd(II) and Rh(III) from coated ceramic honeycomb using Cyanex 923

Metal ions	Composition of solution [H1] (mg/l)	Composition of solution [H2] (mg/l)	Composition of solution [H3] (mg/l)	Recovery (%)	Purity (%)
Pd	19.8 ± 0.6	<0.05	19.7 ± 0.5	99.5	99.49
Rh	3.46 ± 0.5	3.45 ± 0.5	<0.1	99.7	98.57

Note: '±' refers to the standard deviation

<0.05/<0.1 refers to less than the detection limit of the corresponding metal ion.

Table 3A.9. Recovery of Pd(II) from spent palladium coated alumina catalyst using Cyanex 923

Metal ions	Composition of solution [C1] (mg/l)	Composition of solution [C2] (mg/l)	Composition of solution [C3] (mg/l)	Recovery (%)	Purity (%)
Pd	9.91 ± 0.4	0.10	9.78 ± 0.6	98.6	98.99
Al	1203 ± 6	1208 ± 7	<0.1	100	99.99

Note: '±' refers to the standard deviation

<0.05/<0.1 refers to less than the detection limit of the corresponding metal ion.

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CHAPTER IIIB

PERMEATION STUDIES ON Pd(II) USING SUPPORTED LIQUID MEMBRANE IMPREGNATED WITH CYANEX 923

A supported liquid membrane (SLM) is one of the three-phase liquid membrane systems in which the membrane phase (liquid) is held by capillary forces in the pores of microporous polymeric or inorganic film. The immobilized liquid is a membrane phase and a microporous film serves as a support for the membrane. Usually SLMs are based on hydrophobic organic solvent immobilized in a polymeric membrane separating two aqueous solutions.

SLM was reported for the first time by Scholander (1) who used thin cellulose acetate filters impregnated with an aqueous haemoglobin solution for oxygen transport. A similar system was reported by Wittenberg (2) for studying the molecular mechanism of oxygen transport. In the 1960s and 1970s, the liquid membrane concept was mostly used in emulsion liquid membranes, when Li (3) patented their application for hydrocarbons separation. However in the beginning of the 1980s, there was an increase in research interest for the SLMs as they were being used to solve an increasing number of separation problems, including metals and organic compounds and the resolution of stereoisomers. The unique flexibility and ease of preparation of SLMs in various configurations has resulted in their applications in diversified fields where selective and efficient separation methods are necessary namely hydrometallurgy, biotechnology, wastewater treatment, analytical and environmental chemistry and pharmaceutical industry.

In all the types of membrane extraction techniques, the membrane separates the sample phase (often called source or feed solution) from the receiving or strip phase and the analyte molecules pass through the membrane from the donor to the acceptor by a process called pertraction (permeation-extraction). Membrane extraction techniques can be divided into two main categories: porous and nonporous membrane techniques (4). A clear difference between these two is that the selectivity for porous membrane processes is mainly based on pore size and pore size distribution. A nonporous membrane can be either a porous membrane impregnated with a liquid or a solid, like silicone rubber. In both the cases, the chemistry of the membrane material can influence the selectivity and permeability coefficient of the process. Extraction technique based on non-porous membrane, generally, offers a high degree of selectivity and enrichment power. It finds application in extraction methods based on supported liquid membrane (SLM), microporous membrane, polymeric membrane and membrane with a sorbent interface (5).

Membrane technology is often used to recover metals from waste streams or to remove the metal contaminants from the environmental samples. For the efficient removal of cations and anions, the selection of an appropriate membrane is critical. The important characteristics that need to be considered in the selection of a membrane include the stability towards solutions of varying pH and harsh chemical and physical treatment. Besides this, the membrane must be durable and stable at high temperatures. Membranes are manufactured using inert materials such as polytetrafluoroethylene (PTFE) and polyvinylidene fluoride (PVDF) (5). Three different physical realizations of SLM modules generally reported are flat, spiral and tubular (6, 7). For flat modules, a groove is machined in each block and liquid connections are provided at both the ends. A carrier impregnated membrane is clamped between the blocks, forming a channel at both the sides of the membrane. An ideal membrane support is the one that gives high solute permeation. Generally, thin membranes with small pores (~0.2 μm) and polyethylene backing are used (8, 9). This facilitates mass transfer and at the same time helps to retain the impregnated liquid firmly to avoid deformation which occurs due to small pressure changes in the system.

Supported liquid membrane separation combines solvent extraction and stripping process (re-extraction) in a single step. The main advantages of SLMs are the small amounts of organic phase and extractants (carrier) used, one-step mass transfer, the possibility of achieving high separation factors, concentration of extracted compound(s) during separation, and low separation costs.

In an SLM system an organic support material by capillary forces, separates two aqueous solutions, the feed (donor) and the strip (receiving, acceptor) phase (figure 3B.1). The compounds are separated form the aqueous sample feed phase into an organic solvent immobilized in a support diffusing through the membrane phase, and then they are continuously back extracted to the other side of the membrane into the strip phase. The driving force is the difference in concentration of the compounds between the phases.

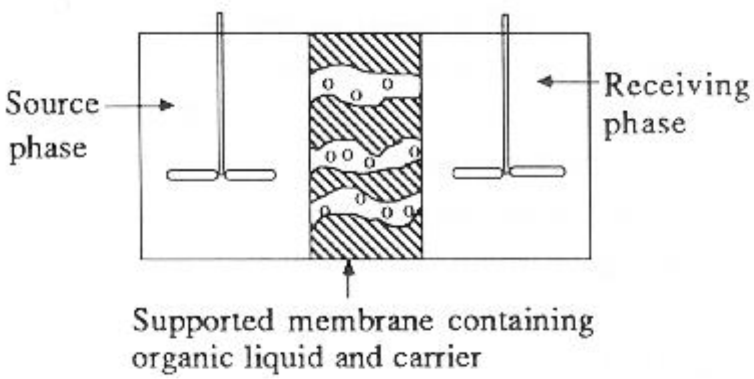

Figure 3B.1: Schematic diagram representing the pertraction across the SLM

The transport of the substance from the feed solution to the strip side can be divided into several stages (figure 3B.2) -

(a) Diffusion of Pd(II) in the non-stirred boundary layer (feed solution-membrane interface).

(b) Formation of Pd(II)-Cyanex 923 complex at the feed solution-SLM interface.

(c) Diffusion of the complex formed, Pd(II)-Cyanex 923, through the supported liquid membrane.

(d) Stripping of Pd(II) from the Pd(II)-Cyanex 923 complex at the SLM-stripping solution interface.

(e) Diffusion of Pd(II) in the non stirred boundary layer (membrane-stripping solution interface).

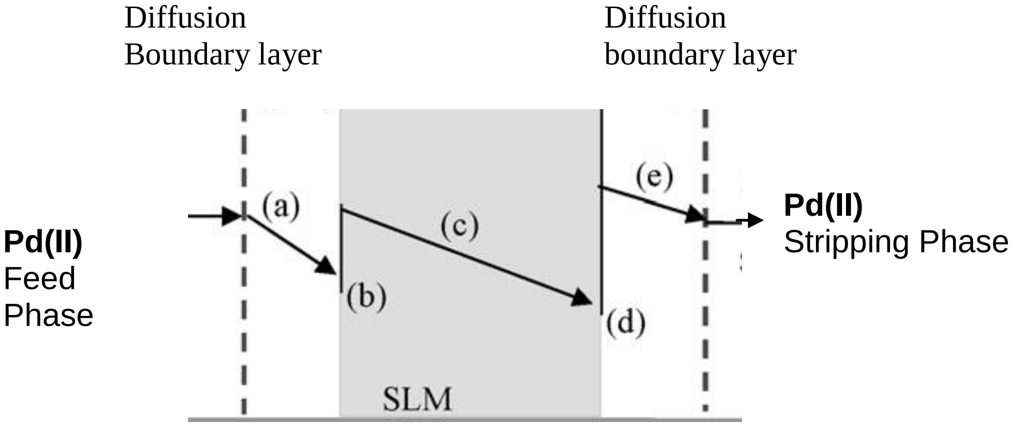

Figure 3B.2: Graphical representation of Pd(II) transfer through the SLM

Nevertheless, there are some problems limiting the practical applications of SLMs. The main problem is the instability of the liquid membrane, caused by leakage and/or losses of membrane phase components during transport process. Not only the properties of a membrane are important but the operating conditions are equally important. Process parameters such as pH and fluid turbulence affect the rate at which the ions are transported across the membrane. The concentration of ions and the stirring rate of solutions in both the feed and receiving phases must be controlled to maintain the steady-state conditions at the boundary layers of the membrane.

Literature survey revealed a number of reports on the supported liquid membranes containing a variety of extractants like chelating agents (10-13), high molecular weight amines (14-19) and organophosphorus extractants (20-23) as mobile carrier. But chelating agents and high molecular weight amines have limited usage due to the drawbacks like water solubility and poor selectivity.

The efficiency of supported liquid membranes containing Cyanex extractants as a mobile carrier for the pertraction of various groups of metal ions has been extensively studied and a voluminous literature has accumulated on the subject. Following paragraphs summarise the literature on SLMs using Cyanex extractants as mobile carrier.

Madaeni et al. (24) carried out selective transport of Bi(III) using the supported liquid membrane containing Cyanex 301 as carrier. The interferences of cations on the selective transport of Bi(III) were eliminated by using pyrophosphate ions as masking agent. The selective transport of Bi(III) through the membrane was superior to that of solvent extraction or bulk liquid membrane. The system can be applied to the samples containing low bismuth concentration. Aguilera and research group (25) studied the extraction of Bi(III) from synthetic solution using Cyanex 921 impregnated SLM. The concentration of Cyanex 921 in the SLM which produced the maximum Bi(III) extraction was observed to be 0.3 mol L^{-1}. The performance of H_2O and 0.2 mol L^{-1} H_2SO_4 as stripping solutions was evaluated and only later enabled Bi(III) transfer. Santiago et al. (23) reported a systematic study on the separation of Bi(III) and Sb(III) by the SLM using Cyanex 921 as the carrier. A study on As(V) transfer through SLM impregnated with Cyanex 921 was conducted by Perez et al. (26). Transport of As(V) from 2 mol L^{-1} H_2SO_4 solution was studied as a function of parameters such as the nature of the stripping solution, extractant concentration and stirring rate. Quantitative stripping of As(V) was observed with Na_2SO_4. The highest As(V) transfer was found at a Cyanex concentration of 0.12 mol L^{-1}.

Supported liquid membranes deploying Cyanex extractants have also been investigated for f-block elements. Some of the reports are cited below. Valls and group (27) investigated in detail the transport of lanthanides between chloride solutions by a facilitated transport through an SLM containing Cyanex 925. The influence of various parameters affecting the transport of neodymium was determined. Hoshi and co-workers (28) studied the transport of americium and europium across an SLM employing Cyanex 301 as the carrier. A large difference in the transport rate between Am and Eu was obtained at low pH, though a long time was required for metal transport. Sawant and associates (29) examined the transport of U(VI) from nitrate medium across a FSSLM and hollow fibre supported liquid membrane (HFSLM) deploying Cyanex 272 as a mobile carrier. Oxalic acid was used as the strippant for both the systems. Application of the proposed method was extended for the removal of uranium from phosphate waste generated in fuel reprocessing plant. Sawant and research group (30) examined the transport behaviour of Pu(IV) through FSSLM. The developed method was also applied to HFSLM and compact supported liquid membrane flow cell (CSLMFC). Bhattacharyya and others (31) investigated the transport behaviour of trivalent actinides (Am(III) and Cm(III)) and lanthanides (La(III), Eu(III), Tb(III), Ho(III), Yb(III) and Lu(III)) through a polypropylene based SLM containing Cyanex 301 in n-dodecane as a carrier. The trivalent actinides were quantitatively separated from lanthanides by the proposed membrane based method. The transport data of actinide separation correlated well with the results of the solvent extraction studies.

Joshi and others (32) studied the transport of U(VI) and Eu(III) across the SLM. The membrane was impregnated with DEHPA and a neutral organophosphorus oxo donor dissolved in n-dodecane. The different organophosphorus oxo donors studied for synergism were TBP, di-butyl butyl phosphonate, TOPO and Cyanex 923. The prepared membranes were evaluated for U(VI) and Eu(III) transport from phosphoric acid feed to receiver compartment containing $(NH_4)_2CO_3$. Singh and group (33) applied the SLM technique for the separation of U(VI) from phosphoric acid medium using a binary mixture of PC-88A and Cyanex 923 in n-dodecane as a carrier and $(NH_4)_2CO_3$ as a receiving phase. Stability of the membrane against the leaching of the extractant and stability of the membrane support was also investigated. Biswas and group (22) studied the permeation of U(VI) from nitrate medium across the SLM using Cyanex 272 either alone or in combination with neutral donors namely Cyanex 923, TBP and tris(2-ethylhexyl) phosphate (TEHP) dissolved in n-paraffin as carrier. The transport behaviour of U(VI) was compared with other derivatives of phosphoric acids like PC-88A and di-nonyl phenyl phosphoric acid (DNPPA) under identical conditions and the order followed was Cyanex 272> PC-88A>DNPPA. Presence of the neutral donors in carrier showed significant enhancement in U(VI) permeation in the order: Cyanex 923>TBP>TEHP. In another publication (34) they reported the transport of U(VI) from HNO_3 medium through SLM. Receiver phases like H_2SO_4, oxalic acid, citric acid and Na_2CO_3 were evaluated and 2 mol L^{-1} H_2SO_4 was found to be most effective. The synergistic mixture of DNPPA and Cyanex 923 was used to recover U(VI) from uranyl nitrate raffinate solution.

In the last two decades a voluminous literature has appeared on the use of Cyanex extractants as impregnants for the permeation of transition metal ions. Kanungo and Mohappatra (35) proposed a model to describe the rate of transport of metal complex species through SLM under different conditions. They used the Zn(II)-Cyanex 272 system for the study. In another study (36) the kinetics of the permeation of Zn(II) through SLM with Cyanex 272 in kerosene under different experimental conditions. At high carrier concentration and high pH the Zn(II) flux was described by the diffusion of $ZnL_2(HL)$ and $ZnL_2(HL)_2$ species. Daoud et al. (37) investigated the permeation of Cd(II) from phosphate medium through SLM consisting of a flat disk cellulose nitrate membrane immobilizing Cyanex 301 in kerosene as carrier. The difference in the kinetic behaviour of Cd(II), Cu(II), and Zn(II) when mixed together was used to improve the selective separation of Cd(II) by the investigated SLM system. The conditions for the use of the system in pollution control of the environment with heavy metals produced from phosphate wastewater streams were also discussed. Walawska and Kowalski (38) reported the transport of Cr(VI) through SLM and the separation of Cr(VI) and Cr(III) across SLM containing Cyanex 921 as a carrier. The kinetic parameters as well as degree of removal of Cr(VI) through SLM were studied as a function of acidity and Cr(VI) concentration in source phase, concentration of Cyanex 921 in organic phase and composition of receiving phase.

Alguacil et al. (39) studied the carrier-facilitated membrane transport of Cr(VI) from chloride medium across a FSSLM using Cyanex 923 as the carrier. The permeation of Cr(VI) was investigated under various experimental conditions namely stirring speed of the feed phase, initial metal and carrier concentration, organic phase diluent, HCl concentration in the feed phase, composition of the stripping phase and support characteristics. Alguacil and Alonso (40) investigated Fe(III) transport across an SLM using Cyanex 921 as carrier. They reported a model describing the transport mechanism which consists of a diffusion process through a source aqueous diffusion layer, a fast interfacial chemical reaction and diffusion of $HFeCl_4.L_2$ (L represents the extractant) through the membrane. The behaviour of Cyanex 921 was studied with respect to other organophosphorus extractants. In another report (41) they investigated the transport of Zn(II) across SLM impregnated with Cyanex 923. The influence of source phase stirring speed, membrane composition and metal concentration on zinc transport was checked. Gega and associates (42) reported a competitive transport of an equimolar mixture of Co(II) and Ni(II) in sulphuric acid medium across SLM and hybrid liquid membranes (HLM). In both types of membranes DEHPA, Cyanex 272, Cyanex 301 and Cyanex 302 were used as ion carriers. In the HLM processes lower metal ion fluxes than in SLM processes were observed. They found that higher separation coefficients were observed for HLM than for SLM. Alguacil et al. (43) studied the transport of Cd(II) through a polymer immobilized liquid membrane (PILM) using Cyanex 923 as carrier. Factors affecting Cd(II) permeability namely stirring speed of the source phase, extractant concentration in the membrane phase, metal ion, HCl and H_3PO_4 concentration in the source phase were evaluated.

Bhandare and Argekar (44) carried out the transport of Hg(II) from chloride medium through a FSSLM containing Cyanex 471X as the mobile carrier in kerosene. Sodium thiocyanate solution was used as receiving phase. Cyanex 471X selectively and efficiently transported Hg(II) in the presence of other associated metal ions. The developed process was demonstrated to selectively recover mercury from waste samples and mercurochrome solution. Kozolowski and Gaida (45) used SLM for selective separation and concentration of heavy metal ions. They discussed the possibility of the separation of Co(II) and Ni(II) using SLM containing Cyanex 272, as well as of Zn(II) and Cd(II) using polymer inclusion membrane containing orthonitrophenylpentyl ether and TOA. Alguacil and Alonso (46) reported the transport of Cr(VI) through a FSSLM impregnated with Cyanex 923 as the carrier. The permeation of the metal ion as a function of various experimental variables was studied. They investigated the selectivity of Cyanex 923 based FSSLM towards different metal ions and the behaviour of the system against other carriers. In another publication (47) transport of Cr(VI) through a FSSLM containing Cyanex 921 was studied. The permeation of the metal ion was investigated as a function of various experimental variables. They also studied the transport of Cr(VI) through FSSLM containing Cyanex 923 (48). The permeation of the metal was investigated as a function of various experimental variables such as hydrodynamic conditions, concentration of Cr(VI) and HCl in the feed phase, Cyanex 923 concentration and diluent in the membrane and strippant concentration in the receiving phase. They used hydrazine sulphate in the receiving phase to reduce Cr(VI) to less toxic Cr(III). The alkylphosphinic acid Cyanex 272 was impregnated on the polymeric inclusion membrane support made up of cellulose triacetate and o-nitrophenyl pentyl ether. The impregnated membrane was investigated for the separation of Zn(II) and Cd(II) from dilute chloride solutions (49). The recovery of Co(II) (50) and its separation from Ni(II) (51, 52) was achieved by pertraction technique using SLM containing Cyanex 302 as carrier. The method was applied to industrial leach liquor for the recovery of Co(II) and Ni(II).

Alguacil and Alonso (53) also investigated the influence of the membrane diluent on cadmium transport across FSSLM using Cyanex 921 and Cyanex 923 as carriers and Durapore GVHP4700 as the solid support. Rodriguez and co-workers (54) studied the extraction of Cd(II) from HCl medium using Cyanex 923 in Solvesso 100 and implemented the results onto an SLM. The influences of feed phase stirring speed, membrane composition and metal concentration on cadmium transport were investigated. Alguacil and Tayibi (55) studied the transport of Cd(II) from a high-salinity chloride medium across a FSSLM containing Cyanex 923 in Solvesso 100 supported on a PVDF membrane. Alonso and group (56) investigated the transport of Cd(II) from chloride medium through a FSSLM using Cyanex 923 as an impregnant. Various phase variables namely hydrodynamic conditions, concentration of Cd(II) and HCl in the feed phase, carrier concentration and diluent in the membrane phase were studied. The separation of Cd(II) against Zn(II), Fe(III), Co(II) and Cu(II) was evaluated. Swain and associates (57) compared the extraction of Co(III) from sulphate medium by SLM and solvent extraction. In both the processes effect of different parameters such as feed solution pH, Cyanex 272 concentration, cobalt concentration in the feed phase, stripping acid concentration on the cobalt flux and cobalt distribution coefficient was investigated. In another report (58) they studied the permeation rate of Co(II) and Li(II) from sulphate medium using SLM impregnated with Cyanex 272. The microporous hydrophobic PVDF film was used as the solid support. They studied the effect of various parameters namely speed of rotation, pH in feed solution, Cyanex 272 concentration in membrane, Co(II) and Li(I) concentration in feed solution and strippant concentration on Co(II) flux and Li(I) flux. Parhi and Sarangi (59) separated copper, zinc, cobalt and nickel ions from synthetic leach liquor using SLM. They used LIX 84I, TOPS-99 and Cyanex 272 as the mobile carrier. Copper was first separated using LIX 84I followed by zinc using TOPS-99 and cobalt using Cyanex 272. Parhi and co-workers (60) reported the extraction efficiencies of DEHPA, PC-88A and Cyanex 272 for cadmium in SLM. The effect of various parameters was investigated. The extraction of cadmium using the phosphoric acid derivatives followed the order DEHPA>PC-88A>Cyanex 272. Rathore and associates (61) reported a process to remove and recover cadmium from waste water by solvent extraction and SLM using Cyanex 923 as extractant. To improve the stability of SLM and scale up for continuous operation the performance of hollow fibre strip dispersion technique for the recovery of Cd(II) was also examined. Swain et al. (62) separated Co(II) and Li(I) from a lithium ion battery (LIB) industry waste by an SLM process. The extractants Cyanex 272 and DP-8R and mixture of the two were used as the mobile carrier. The order followed was - mixed extractant system>Cyanex 272>DP-8R.

Sastre and group (63) investigated the permeation of Au(I) through an SLM impregnated with various extractants. High selectivity in the separation, through SLM, of Au(I) against different metal-cyano complexes ($Ag(CN)^{2-}$, $Cu(CN)_4^{3-}$, $Zn(CN)_4^{2-}$ and $Fe(CN)_6^{3-}$) was achieved. Alguacil et al. (64) investigated the permeation of Au(III) across an SLM impregnated with Cyanex 923 in n-decane. They proposed a model in which the transport was by diffusion process through the feed aqueous diffusion layer and rapid interfacial chemical reaction and diffusion through the membrane. High selectivity in the separation of Au(III) with respect to the PGMs was achieved. In another report (65) they used Cyanex 923 for the transport of gold either from cyanide or chloride media across a polymer immobilized liquid membrane. Water and sodium thiocyanate were used as effective receiving phase with cyanide and chloride feed phase, respectively. Fontas et al. (66) impregnated the SLM with Cyanex 471X for the separation and concentration of palladium from feed chloride solution containing SCN^-. They reported that among the various solvents tested in the report, the aliphatic diluent decaline provided the best results in terms of the stability of the SLM. Alguacil (67) studied the transport of Au(III) from HCl medium across SLM containing Cyanex 921. Transport of the metal ions was investigated as a function of various experimental variables. Author checked the selectivity of the proposed method towards different base metals. Alguacil and Alonso (68) studied the transport of $Au(CN)^{2-}$ across an SLM using a mixture of Primene JMT and Cyanex 923. The transport of Au(I) was described as a diffusion process through the feed aqueous layer, rapid interfacial chemical reaction and diffusion of $HAu(CN)_2RL$ and $HAu(CN)_2RL_2$ (R= amine and L= Cyanex 923) through the membrane. In another report (69) they investigated the transport of Au(I) from cyanide medium and Au(III) from chloride medium through SLM containing Cyanex 921.

The reviewed literature revealed that Cyanex 923 has not been explored for recovery of palladium using flat sheet supported liquid membrane based extraction technique. Studies conducted in the chapter IIIA clearly demonstrated the affinity of Cyanex 923 for Pd(II). Keeping this in mind, a flat-sheet supported liquid membrane containing Cyanex 923 as carrier was designed. The effects of various process parameters such as concentration of sulphuric acid and palladium in the feed phase, concentration of the carrier in the organic phase, concentration of $HClO_4$ in the stripping phase, stirring speed of aqueous phases, nature of membrane solvent and time of transport were evaluated. To test the efficiency of Cyanex 923-impregnated flat-sheet supported liquid membrane for the recovery of palladium, the developed method was applied to the digested solution of coated ceramic honey comb.

Experimental Procedure

In the present investigations, the hydrophobic membrane was impregnated with the carrier solution containing appropriate concentration of Cyanex 923 diluted with toluene. The membrane was immersed in the carrier solution for 24 hours and then allowed to drip till it was dry in order to ensure the complete removal of toluene and excess carrier. It was ascertained that prolonged immersion of membrane for 48 hours in the carrier solution displayed insignificant change in the percentage transport of Pd(II).

The transport experiments were carried out by placing the flat-sheet supported liquid membrane (FSSLM) in a two-compartment permeation cell made of methacrylate. The effective membrane area was 7.35 cm^2 and the volume of feed and receiving solutions was 75 mL each. The feed and receiving phases were mechanically stirred to avoid the conditions of concentration polarization at the membrane interface and in the bulk of the solution. In all the experiments, the stirring speed of 600 min^{-1} was maintained for both source and receiving phases. The exception being in the experiments where the effect of stirring speed on permeation was investigated. Agitation was performed in both the compartments by using Teflon impellers having a diameter of 5 mm. Perecent transport of palladium was determined by monitoring palladium concentration in the source and receiving phase as a function of time. All the data reported is based on a minimum of two determinations. The flux and the permeability coefficient are the two characteristic values evaluated for the membrane. The permeation coefficient (P) was computed using:

$$\ln \{[Pd]_t / [Pd]_o\} = - (A / V) P \times t \quad (1)$$

where A is the effective membrane area (cm^2), V is the volume of the source phase (cm^3), $[Pd]_t$ and $[Pd]_o$ are the concentrations of palladium (mg L^{-1}) in the source phase at elapsed time t and zero (s), respectively.

The permeability of Pd(II) across the FSSLM is described using diffusional parameters. The interfacial flux due to the chemical reaction has not been considered, since the chemical reaction is assumed to occur instantaneously compared to the diffusion processes (70). The overall membrane flux can be derived by applying Fick's First Diffusion Law to the diffusion layer in feed side and the membrane (71) with the assumption that the distribution coefficient of Pd(II) between the membrane phase and the receiving phase is much lower than that between the feed phase and the membrane. The concentration of the metal-extractant complex in the membrane phase on the receiving solution side may be considered negligible as compared with that on the feed solution side. Thus, at steady state, the diffusional fluxes at the feed aqueous boundary layer J_f and in the membrane phase J_m are equal.

$$J_f = J_m = J \quad (2)$$

The diffusional flux is expressed as (72, 73),

$$J = P [Pd]_0 \quad (3)$$

where J is the initial flux calculated from the permeability coefficient P and the initial palladium concentration $[Pd]_0$ in the feed phase.

Results and Discussion

The transport of Pd(II) through the SLM impregnated with Cyanex 923 as carrier involves diffusion of Pd(II) from the aqueous feed solution to the feed-membrane interface. The interaction between the Pd(II) and Cyanex 923 takes place and forms an palladium-Cyanex complex, which is transported through the membrane to membrane-receiving phase interface. The palladium-Cyanex complex breaks at the membrane-receiving phase interface and Pd(II) is stripped into the receiving phase. The regenerated Cyanex 923 molecule diffuses back to the feed-membrane interface to complete the cycle (figure 3B.3). The impact of different operational parameters on the transport through the supported liquid membrane was investigated. It may be mentioned here that the percent transport of Pd(II) across the membrane used at different times was found to be fairly reproducible.

Effect of carrier concentration

It is generally seen that transport of metal ion through the supported liquid membrane depends on the concentration of carrier molecule in the membrane phase (74, 75). Therefore, to understand the effect of Cyanex 923 concentration on the permeability of Pd(II), studies were carried out with varying concentration of Cyanex 923 from 0.2 mol L^{-1} to 1.2 mol L^{-1} in toluene. Figure 3B.4 shows the transport profile of palladium at different carrier concentrations. The Permeability co-efficient values at different Cyanex 923 concentrations

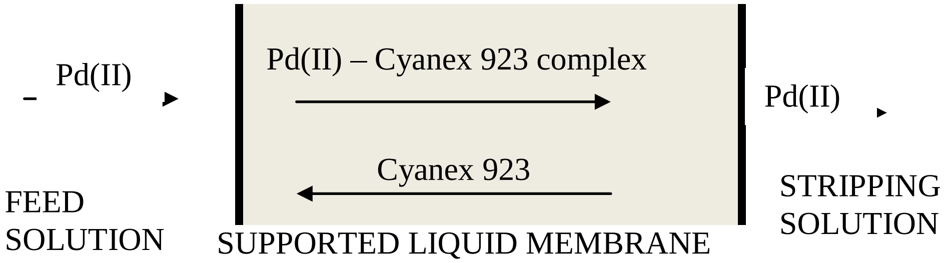

Figure 3B.3: Schematic diagram of Pd(II) transfer process through SLM using Cyanex 923 as carrier.

tabulated in table 3B.1, revealed a gradual increase in the permeability of Pd(II) with the increasing Cyanex 923 concentration up to 1.0 mol L^{-1}. Beyond this a constant value of permeability co-efficient (1.24×10^{-2} cm s^{-1}) was observed.

Effect of time

Figure 3B.5 shows the time dependence of Pd(II) transfer through the SLM under optimal conditions. It is obvious from the figure that the transport of Pd(II) from source phase into the organic phase is almost complete after 85 minutes. For all further studies stirring of both the phases was carried out for 90 minutes.

Effect of sulphuric acid concentration in feed phase

Distribution studies carried out in chapter IIIA indicated that H_2SO_4 medium favours the extraction of Pd(III) from the aqueous phase to the organic phase containing Cyanex 923. The permeation studies were thus carried out from sulphuric acid medium. The effect

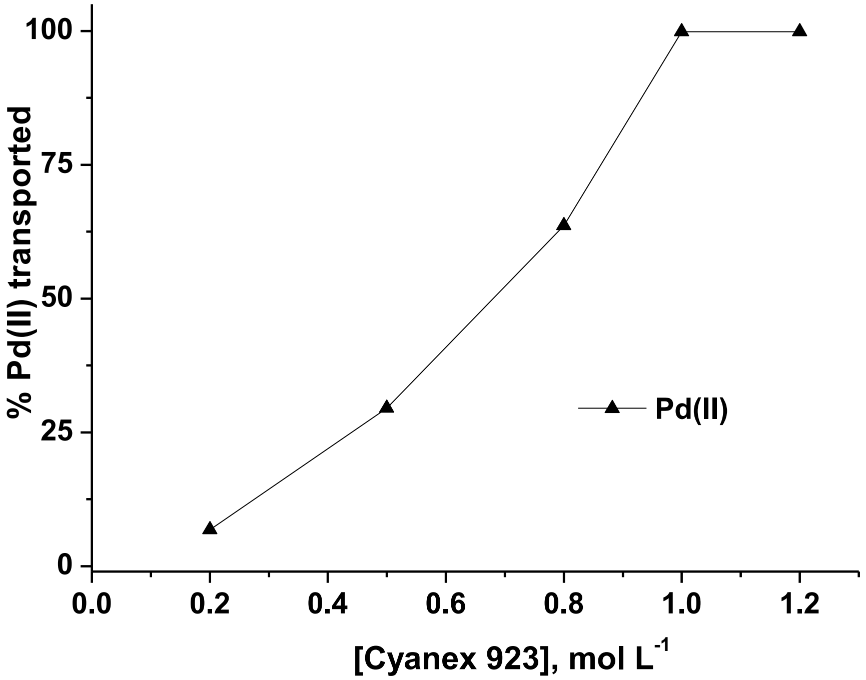

Figure 3B.4: Effect of Cyanex 923 concentration on the transport of Pd(II)

Conditions

Feed phase: 1.0×10^{-3} mol L^{-1} Pd(II) at 5.0 mol L^{-1} H_2SO_4

Receiving phase: 5.0 mol L^{-1} $HClO_4$

Stirring time: 120 minutes

Stirring speed of feed and receiving phase: 500 min^{-1}

Membrane phase: PVDF membrane containing varying concentration Cyanex 923 in toluene

Table 3B.1. Effect of carrier concentration on the permeability of Pd(II).

Carrier concentration (Cyanex 923), mol L^{-1}	Permeability ($x10^2$, cm s^{-1})
0.20	0.013
0.50	0.066
0.80	0.191
1.0	1.24
1.2	1.24

Conditions

Feed phase: 1.0×10^{-3} mol L^{-1} Pd(II) at 5.0 mol L^{-1} H_2SO_4

Receiving phase: 5.0 mol L^{-1} $HClO_4$

Stirring time: 120 minutes

Stirring speed of feed and receiving phase: 500 min^{-1}

Membrane phase: PVDF membrane containing 1.0 mol L^{-1} Cyanex 923 in toluene

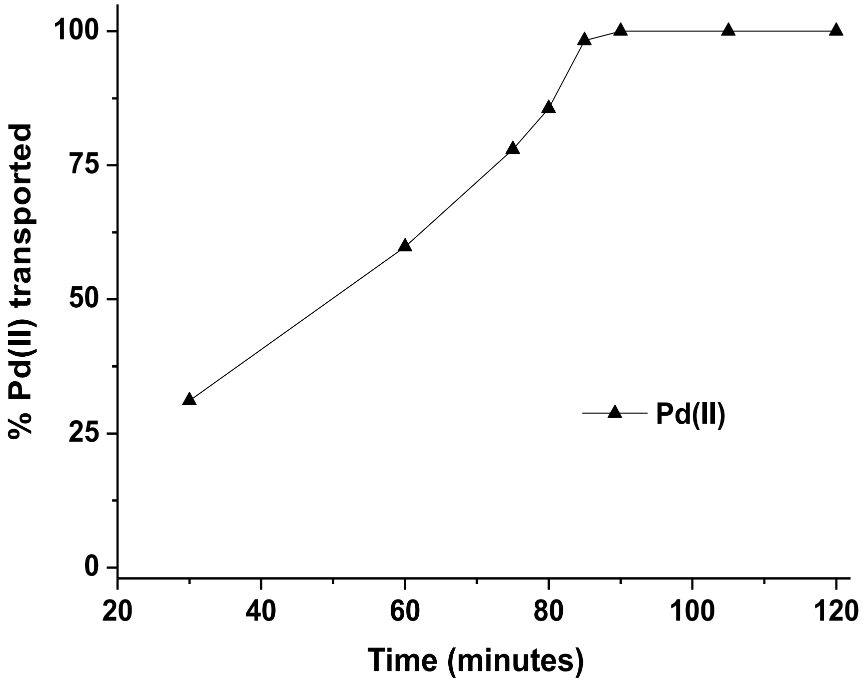

Figure 3B.5: Effect of the stirring time on the transport of Pd(II)

Conditions

Feed phase: 1.0×10^{-3} mol L^{-1} Pd(II) at 5.0 mol L^{-1} H_2SO_4

Receiving phase: 5.0 mol L^{-1} $HClO_4$

Stirring speed of feed and receiving phase: 600 min^{-1}

Membrane phase: PVDF membrane containing 1.0 mol L^{-1} Cyanex 923 in toluene

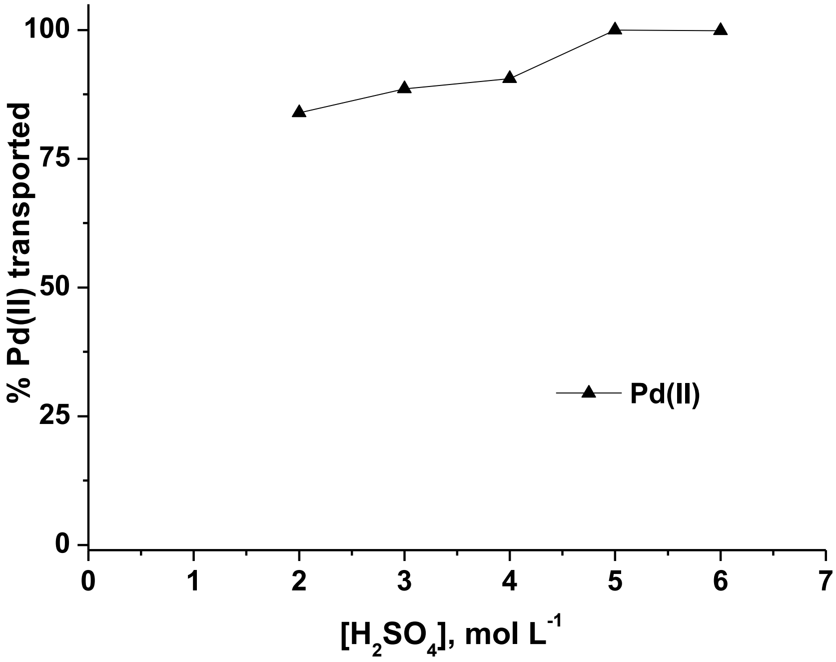

Figure 3B.6: Effect of H_2SO_4 concentration in feed phase on the transport of Pd(II)

Conditions

Feed phase: 1.0×10^{-3} mol L^{-1} Pd(II) at varying acid concentration

Receiving phase: 5.0 mol L^{-1} $HClO_4$

Stirring time: 90 minutes

Stirring speed of feed and receiving phase: 600 min^{-1}

Membrane phase: PVDF membrane containing 1.0 mol L^{-1} Cyanex 923 in toluene

of H_2SO_4 concentration in the feed phase on the transport of Pd(II) was investigated using FSSLM containing 1.0 mol L^{-1} Cyanex 923 in toluene and 5.0 mol L^{-1} $HClO_4$ as strippant. The feed phase conditions were maintained as 1.0 x 10^{-3} mol L^{-1} Pd(II) at varying H_2SO_4 concentration (2.0 to 6.0 mol L^{-1}). The two phases were stirred at a speed of 600 min^{-1} for a period of 90 minutes. From figure 3B.6, it is evident that increasing sulphuric acid concentration causes an increase in Pd(II) transport up to 5.0 mol L^{-1}. Further increase in sulphuric acid concentration does not play much role in the transport profile. All further studies were conducted at 5.0 mol L^{-1} H_2SO_4 in feed phase.

Effect of the stirring speeds of feed and receiving phases

The influence of the stirring speed of the feed phase and receiving phase on the transport of Pd(II) was studied using FSSLM containing 1.0 mol L^{-1} Cyanex 923 in toluene. The feed and receiving phase conditions were 1.0 x 10^{-3} mol L^{-1} Pd(II) at 5.0 mol L^{-1} H_2SO_4 and 5.0 mol L^{-1} $HClO_4$, respectively. The effect of varying stirring speed (40 - 700 min^{-1}) of both the phases was studied for a transport time of 90 minutes (figure 3B.7). Maximum transportation of Pd(II) was achieved at the stirring speed of 600 min^{-1} and remained constant thereafter. For all further studies stirring speed of 600 min^{-1} was used for both the phases.

Effect of the concentration of receiving phase solution

The results of stripping studies carried out in chapter IIIA indicated that malonic acid, acidic solution of sodium salt of DMG and $HClO_4$ are efficient stripping reagents for the recovery of Pd(II) from the loaded organic phase. Out of these $HClO_4$ was selected as a strippant for Pd(II) for the permeation studies. The pertraction studies were conducted by varying the concentration of $HClO_4$ (1.0 – 6.0 mol L^{-1}) as the receiving phase for a contact time of 90 minutes (figure 3B.8). The results reveal that maximum stripping of Pd(II) was achieved using 5.0 mol L^{-1} $HClO_4$. Further, increase in $HClO_4$ molarity in the receiving phase showed insignificant change in stripping of Pd(II). Based on this study, 5.0 mol L^{-1} $HClO_4$ was selected as the strippant concentration for the receiving phase.

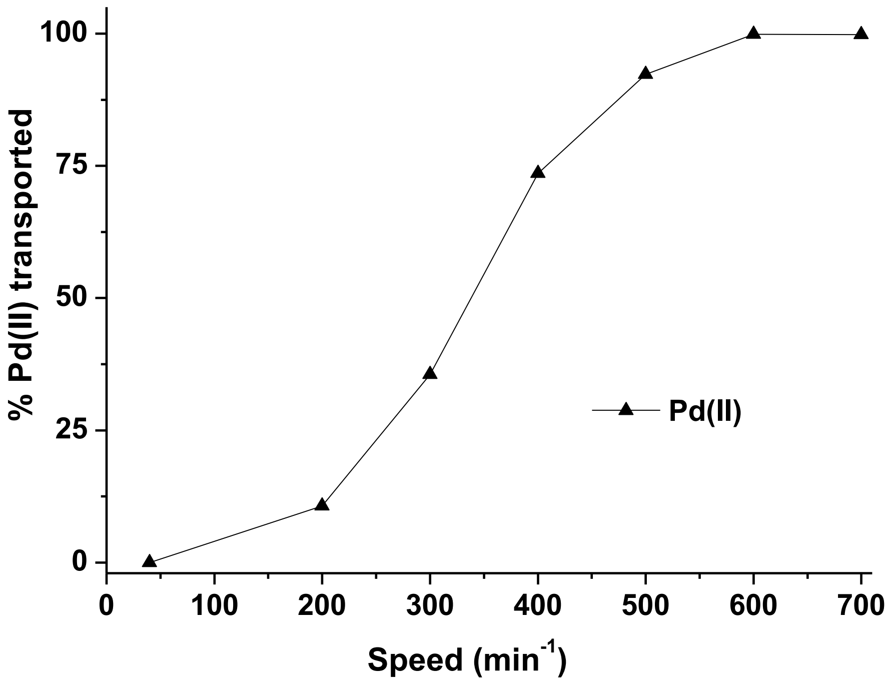

Figure 3B.7: Effect of the stirring speed on the transport of Pd(II)

Conditions

Feed phase: 1.0×10^{-3} mol L^{-1} Pd(II) at 5.0 mol L^{-1} H_2SO_4

Receiving phase: 5.0 mol L^{-1} $HClO_4$

Stirring time: 90 minutes

Membrane phase: PVDF membrane containing 1.0 mol L^{-1} Cyanex 923 in toluene

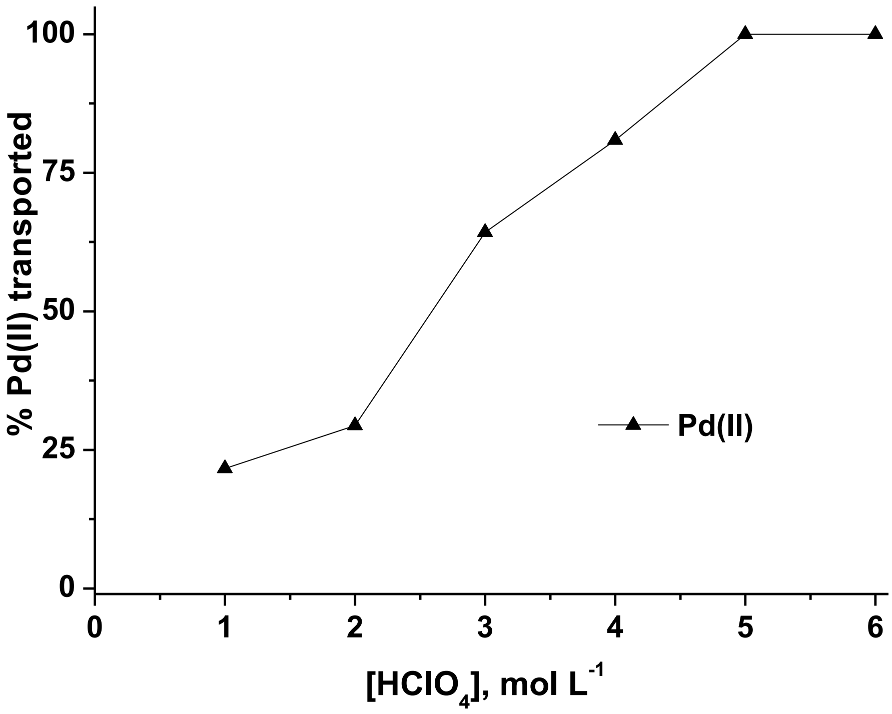

Figure 3B.8: Effect of $HClO_4$ concentration in the receiving phase on the transport of Pd(II)

Conditions

Feed phase: 1.0×10^{-3} mol L^{-1} Pd(II) at 5.0 mol L^{-1} H_2SO_4

Stirring time: 90 minutes

Stirring speed of feed and receiving phase: 600 min^{-1}

Membrane phase: PVDF membrane containing 1.0 mol L^{-1} Cyanex 923 in toluene

Effect of diluent

Besides their high boiling point, low aqueous solubility and wet-ability of polymeric support, the solvents for SLM have to meet two important requirements: satisfactory solubility of ionophore and ability for efficient extraction of the desired metal ion-carrier. To study the permeation of Pd(II), the carrier solutions were prepared in with four diluents of varying nature and dielectric constants namely nitrobenzene, cyclohexane, chloroform and toluene. From the results in table 3B.2, it is evident that Pd(II) showed comparable transport with all the diluents except chloroform. The results are in concordance with the results obtained in chapter IIIA. For all further studies toluene was used as a diluent.

Influence of metal concentration on the permeability of Pd(II)

Permeability of Pd(II) was measured as a function of its concentration in the feed solution. The concentration of Pd(II) in the feed solution was varied from 1.0 x 10^{-4} to 1.0 x 10^{-2} mol L^{-1}, keeping the other parameters constant. Table 3B.3 shows the variation in the Pd(II) permeation coefficient and the initial flux against the concentration of Pd(II) in the feed phase solution. It is evident that with the present experimental conditions the palladium flux increased with the increase of the initial Pd(II) concentration in the feed phase.

Stability of the supported liquid membrane.

It is noteworthy that despite their well known advantages, SLM suffers from poor stability (76, 77). This is mainly due to the loss of carrier and/or membrane solvent from the membrane support. Therefore, it becomes imperative to evaluate the stability of the proposed membrane. One of the approaches generally employed to evaluate the stability of the membrane is by performing several replicate transport experiments. In each cycle, fresh feed (1.0 x 10^{-3} mol L^{-1} Pd(II) at 5.0 mol L^{-1} H_2SO_4) and receiving (5.0 mol L^{-1} $HClO_4$) phases were used, while retaining the same supported liquid membrane. The results (figure 3B.9) indicated a constant percent transport through the membrane for fifteen transport cycles investigated. This shows that the membrane is fairly stable and can be used in long term pertraction experiments.

Table 3B.2. Effect of the nature of various diluents on the transport of Pd(II).

Diluent	Dielectric constant	Percent Transport Pd(II)
Nitrobenzene	35.70	99.73
Cyclohexane	18.3	99.75
Chloroform	4.81	4.53
Toluene	2.44	99.87

Conditions

Feed phase: 1.0×10^{-3} mol L^{-1} Pd(II) at 5.0 mol L^{-1} H_2SO_4

Receiving phase: 5.0 mol L^{-1} $HClO_4$

Stirring time: 90 minutes

Stirring speed of feed and receiving phase: 600 min^{-1}

Membrane phase: PVDF membrane containing 1.0 mol L^{-1} Cyanex 923 in different diluents

Table 3B.3. Variation in the Pd(II) permeation and flux with the initial Pd(II) concentration

Pd(II) concentration (mol L^{-1})	P (cm/s)	J ($x10^8$ mol/cm^2 s)
1.0×10^{-4}	0.0174	0.174
5.0×10^{-4}	0.02	1.0
1.0×10^{-3}	0.0217	2.17
3.0×10^{-3}	0.0238	7.0
7.0×10^{-3}	0.0112	8.0
1.0×10^{-2}	0.0105	10.5

Conditions

Feed phase: 1.0×10^{-3} mol L^{-1} Pd(II) at 5.0 mol L^{-1} H_2SO_4

Receiving phase: 5.0 mol L^{-1} $HClO_4$

Stirring time: 90 minutes

Stirring speed of feed and receiving phase: 600 min^{-1}

Membrane phase: PVDF membrane containing 1.0 mol L^{-1} Cyanex 923 in toluene

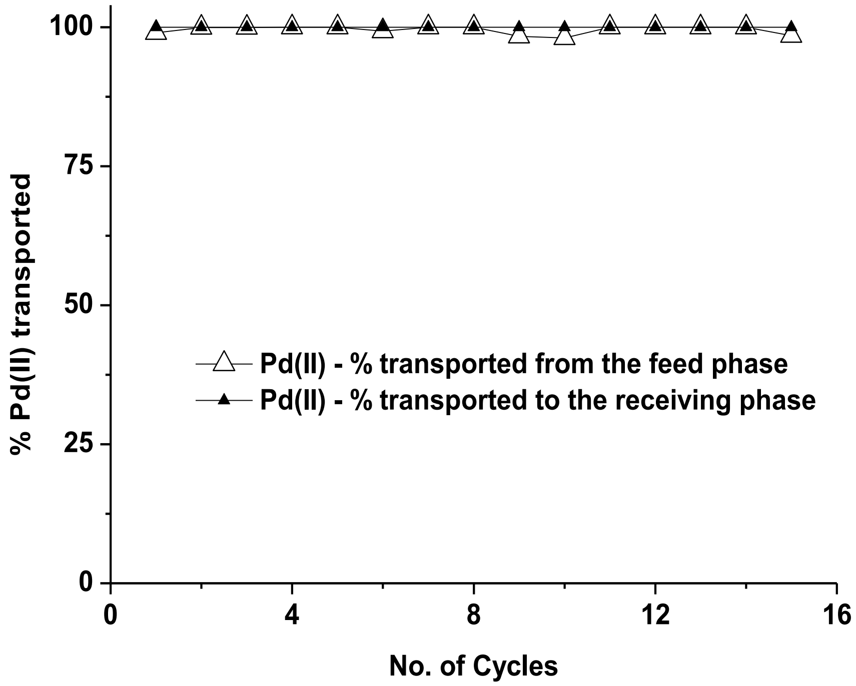

Figure 3B.9: Transport of Pd(II) as a function of the number of permeation cycles

Conditions

Feed phase: 1.0×10^{-3} mol L^{-1} Pd(II) at 5.0 mol L^{-1} H_2SO_4

Receiving phase: 5.0 mol L^{-1} $HClO_4$

Stirring time: 90 minutes

Stirring speed of feed and receiving phase: 600 min^{-1}

Membrane phase: PVDF membrane containing 1.0 mol L^{-1} Cyanex 923 in toluene

The stability of the SLM was also checked with respect to the leaching of the carrier from the membrane phase to feed/receiving phase. For this the feed and the receiving phases were analysed for the phosphorus content after successive fifteen cycles of permeation using the same supported liquid membrane. The analysis indicated negligible phosphorus content (<25 ppb) in both the phases. 25 ppb is the detection limit of ICP-OES. Moreover, the supported liquid membrane was kept in contact with both the phases and the two phases were periodically checked for their phosphorus content. Even after a contact period of fifty days no phosphorus was observed in any of the phases. The negligible releases of Cyanex 923 suggest that it can be used long term pertraction experiments.

Application of the developed SLM system

The developed SLM system was employed to separate palladium and rhodium from a synthetic mixture. 75 mL aliquot of an aqueous solution containing 100 ppm of each Pd(II) and Rh(III) at 5.0 mol L^{-1} H_2SO_4 was taken as the feed phase and 5.0 mol L^{-1} $HClO_4$ as the receiving phase in a permeation cell with SLM containing 1.0 mol L^{-1} Cyanex 923. The feed and the receiving phases were agitated for 90 minutes at a stirring speed of 600 min^{-1}. Both the phases were then analyzed for Pd(II) and Rh(III). The results (table 3B.4) indicated the complete transfer of Pd(II) from the feed phase to the receiving phase whereas Rh(III) was not transported under the experimental conditions and remained in the feed phase.

The present investigations have resulted in the development of a membrane-based extraction technique for the separation and recovery of palladium. The complete permeation of palladium through the supported liquid membrane containing Cyanex 923 as carrier was attained within 90 minutes. Other advantages of the developed technique are low solvent requirement and minimum waste generation. A simple receiving phase (5.0 mol L^{-1} $HClO_4$) was used to recover palladium from the liquid membrane facilitating the regeneration and reuse of the membrane. The developed supported liquid membrane also retained its permeation capacity even after fifteen cycles of reuse. The method was successfully applied to synthetic mixture to recover palladium.

Table 3B.4. Recovery of Pd(II) and Rh(III) from synthetic mixture using SLM impregnated with Cyanex 923

Metal ions	Composition of initial feed solution (mg/l)	Composition of final feed solution (mg/l)	Composition of receiving solution (mg/l)	Recovery (%)	Purity (%)
Pd	101.33 ± 1.2	<0.05	102.69 ± 1.2	100	99.90
Rh	98.0 ± 1.1	99.73 ± 1.2	<0.1	100	99.95

Note: '±' refers to the standard deviation

<0.05/<0.1 refers to less than the detection limit of the corresponding metal ion.

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CHAPTER IV

EXTRACTION STUDIES ON Pt(IV), Ir(III), Rh(III) AND ASSOCIATED METAL IONS USING CYANEX 471X

Since man first discovered fire and invented the wheel there has been a continuous effort through centuries to push back the frontiers of knowledge and this still goes on with marked success. From the very beginning of modern industry the inherent characteristics of platinum metals opened up field for their applications and placed them in a unique place in the history of research and invention. Due to their special chemical and physical properties, the substitution of PGMs by other metals is difficult. Many studies have been conducted on the extraction and separation of PGMs using a variety of extractants (1-5). Keeping the overall scenario on extractants in mind it would not be wrong to mention that the alkylphosphorous compounds still continue to dominate the market. PGMs are soft lewis acids and have strong tendency to complex with soft bases. One such soft base is a sulphur containing extractant of Cyanex series – “Cyanex 471X” (triisobutylphosphine sulphide – TIBPS). Conventionally TIBPS is a sulphur analogue of a phosphine oxide. Because of a lower pKa value it will be able to extract metal ions at a higher acidity than phosphine oxides. The possible utility of Cyanex 471X as an extractant for various metal ions is evidenced by the following text.

Literature review reveals that Cyanex 471X has not been explored for f-block elements. To the best of author’s knowledge a single report is available on the use of Cyanex 471X for f-elements. Yao et al. (6) while studying the extraction behavior of trivalent f-elements with TBP + thiothenoyltrifluoroacetone (HSTTA), Cyanex 471X + thenoyltrifluoracetone (HTTA) and N,N’-dimethyl-N,N’-dihexyl-3-oxapentanediamide + HTTA found HSTTA and Cyanex 471X to be much weaker extractants than the oxo analogs, HTTA and TBP.

Several reports are available on the use of Cyanex 471x for the extraction of transition metal ions. Tandon et al. (7) studied the extraction behavior of Hg(II) and associated metal ions from HNO_3 medium using Cyanex 471X. Effects of different phase parameters have also been investigated. The extracting species has been identified as $Hg(NO_3)_2$.Cyanex 471X. The developed separation conditions have been utilized to recover mercury from paper and pulp industry waste. Singh and group (8) conducted batch experiments on the uptake of Hg(II) from nitrate medium using silica gel impregnated with Cyanex 471X. The effect of different phase variables on the uptake of Hg(II) has been studied. The recycling capacity of the columns was evaluated which revealed an insignificant change in the extraction efficiency of the column up to ten cycles. The practical utility of the columns was demonstrated by decontaminating mercury containing waste effluent. Gotfryd and Szymanowski (9) used di(3,5-

isopropyl)salicylic acid/Cyanex 471X system to carry out distribution studies on Cd(II) and Zn(II). The developed separation procedure was applied to industrial solutions. Moradkhani et al. (10) separated cadmium from zinc using a synergistic mixture of nonylsalicylic acid and Cyanex 471X. Shellsol 2046 was used as a diluent for organic phase and sulphuric acid was employed for quantitative stripping of cadmium. Gotfryd and Cox (11) studied extraction of Cd(II) using an equimolar solution of diisopropylsalicylic acid and Cyanex 471X diluted with Solvesso 150. The extraction of Cd(II) was carried out from the solution obtained by leaching of deposited cadmium carbonate or cadmium cementation sponge heavily contaminated with other components namely zinc. Iron and other contaminants were removed by oxyhydrolysis. Reddy and group (12) employed TOPS 99 (an equivalent of di-2-ethylhexyl phosphoric acid) as an extractant alone and in combination with Cyanex 471X as a synergist. The highest separation factor (1085) was achieved with a combination of 0.05 mol L^{-1} of TOPS 99 and Cyanex 471X each, in a single stage at an equilibrium pH of 4.2. They observed that the Cd-Ni selectivity can be improved by decreasing the A/O phase ration from 1.5 to 1.4.

Precious metals such as gold and silver have also been separated and recovered using Cyanex 471X. Paiva and Abrantes (13) compared the performance of triphenylphosphine (TPP), bis-(pentylthio)-ethane (BPTE) and Cyanex 471X for the extraction of silver from acidic chloride medium. They found that silver was selectively extracted against high contents of iron, copper and lead. The effect of temperature on extraction and stripping was also studied. Paiva and Lemaire (14) used NMR to confirm the Cyanex 471X-Ag ratio when silver was extracted from chloride medium. The coordination shift detected in some nucleus of the organic ligand upon complexation was used to evaluate the ratio. Zuo and Mamoun (15) reported the extraction of Au(III) and Ag(I) by two thiourea based reagents namely nonylthiourea (NTH) and dodecylthiourea (DTH) as well as Cyanex 471X from chloride and nitrate media. The extraction of Au(III) and Ag(I) by the above said reagents was very fast and the equilibration was achieved in less than three minutes. Solvent impregnated resins were prepared from NTH, DTH and Cyanex 471X and macroporous polymers. The extraction of Au(III) from HCl solution by the aforementioned resins was studied. Martinez and group (16) proposed the effectiveness of Cyanex 471X as an extractant for Au(III) from chloride medium. The extraction system was found to be endothermic and the extracted species were defined as $HAuCl_4R$ and $HAuCl_4R_2$, R representing the extractant. Sodium thiosulphate was found effective for the stripping of Au(III) from the loaded organic phase. Mendoza and coworker

(17) investigated the extraction of silver using thiuram sulphides. The extraction efficiencies of these sulphides towards silver were compared with S,S'-12-propanediyl O,O'-dibutyldithiocarbonate (PdBdTC) and Cyanex 471X. Thiuram sulphides were reported to be good extractants for silver in thiosulphate medium. Soldenhoff and Wilkins (18) reported Cyanex 471X to be selective for gold with respect to impurities namely selenium, tellurium, bismuth, lead and copper. The proposed method was tested for the recovery of gold from liquors derived from the oxidative chloride leaching of copper anode slimes. Duche et el., (19) studied the extraction of Au(III) from HBr medium using various organophosphine compounds namely Cyanex 921, Cyanex 923, Cyanex 925 and Cyanex 471X. The extraction reaction was endothermic with Cyanex 471X while exothermic with other extractants. The proposed methods were employed for the analysis of gold in real samples. Pospiech (20) studied extraction of Ag(I) with Cyanex 471X from synthetic nitrate solutions and photographic waste water containing various ions namely iron, sodium and potassium. The influence of the nature of different diluents was checked on the selective extraction of Ag(I) using Cyanex 471X.

From the above literature it is evident that among the Cyanex extractants relatively less attention has been focused on the use of Cyanex 471X for the extraction of various metal ions. Only a few reports are available on its use for the extraction of various PGMs. Mathur et al. (21) used this reagent for the extraction of palladium from nitric acid medium and the extracting species was reported to be $Pd(NO_3)_2$.TIBPS. Duche and associates (22) employed Cyanex 923 and Cyanex 471X for the distribution studies of palladium from bromide medium. They achieved quantitative extraction of palladium with both the extractants. The stoichiometry of the extractable species was found to be 1:2 and 1:1 for Cyanex 923 and Cyanex 471X, respectively. The findings were successfully applied for the analysis of palladium in real samples. The same group of authors in another study (23) explored Cyanex 923 and Cyanex 471X for platinum from bromide medium. Effect of various phase parameters was checked. Both the extractants showed quantitative extraction of Pt(IV). The metal complex species with metal:ligand ratio of 1:1 were extracted with both the extractants. The methods were used for the analysis of platinum in real samples. The same group investigated the extraction of rhodium from bromide medium with toluene solution of Cyanex 923 and Cyanex 471X (24). The quantitative extraction of rhodium was achieved only in the presence of tin for both the extractants. The stoichiometric ratio of Rh(III) with both the extractants was found to be 1:1. The developed methods were successfully applied for the recovery of rhodium from a synthetic solution of spent autocatalyst. Ahmed et al. (25) studied the extraction of Pd(II) with triisobutylphosphine sulphide (Cyanex 471X) in kerosene from nitric acid medium. The stoichiometry of the extracted metal species was found to be $Pd(NO_3)_2$.CYANEX 471X. The stripping of the extracted metal species was carried out using stabilized thiosulphate solution. The results indicated the possibility of separation of palladium from some interfering ions namely Co(II), Fe(III), Cu(II), Cd(II) and Zn(II). The ongoing discussion highlights that only scanty reports are available on the use of Cyanex 471X for the extraction and recovery of PGMs. These studies are mainly focused on bromide medium which may not be convenient for commercialization purpose.

Some of the inherent advantages of Cyanex 471X, discussed earlier, credibly suggest that this extractant scores over many of the other extractants for PGMs which are soft acids. Enticed by this fact the author took up a systematic study on Cyanex 471X for the extraction and separation of platinum, iridium and rhodium. The extractant could not be explored for Pd(II) because of the low solubility of Pd(II)-Cyanex 471X complex. This has been reported earlier also (26). As a first step, the extraction behavior of Pt(IV), Ir(III), Rh(III), Ru(III) and associated metal ions was examined from hydrochloric, sulphuric and nitric acid media employing a solution of Cyanex 471X in toluene. The effect of equilibration time, nature of diluent and concentration of extractant on the distribution was investigated. Based on the distribution data the stoichiometry (metal:extractant) of the extracting species and the loading capacity of the extractants have been investigated. The stripping of extracted metal ions was achieved using some aqueous solutions of varying compositions. The regeneration capacity of the aforementioned extractant and its stability towards long term contact with the acid has been ascertained. The distribution data of metal ions have been utilized to attain some binary separations of topical interest. The separation conditions thus identified have been used to separate and recover Pt(IV), Ir(III) and Rh(III).

Results and Discussion

The extraction behavior of Pt(IV), Ir(III), Rh(III), Ru(III) and some associated metal ions viz: Au(III), Cr(III), Fe(III), Cu(II), Ni(II), Co(II), Fe(II) and Ag(I) using Cyanex 471X is discussed in the following few paragraphs.

Extraction behavior of Pt(IV), Ir(III), Rh(III) and Ru(III) from HCl/H_2SO_4/HNO_3 using 0.10 mol L^{-1} toluene solution of Cyanex 471X

The partition studies for Pt(IV), Ir(III), Rh(III) and Ru(III) were carried out from the three mineral acids, namely hydrochloric, sulphuric and nitric, using 0.10 mol L^{-1} solution of Cyanex 471X (figure 4.1 – 4.3). The acid molarity in each case was varied from 0.10 to 6.0 mol L^{-1}. The maximum extraction of Pt(IV) was achieved at 0.10 mol L^{-1} HCl (82%) and 0.50 mol L^{-1} HNO_3 (55%) followed by a continuous decrease. The extraction of Pt(IV) from H_2SO_4 medium was poor (≤7%) in the investigated range of acid molarity.

The extraction of Ir(III) increased with the increase in the HCl concentration and attained a maximum value (~65%) at 6.0 mol L^{-1} HCl. The maximum extraction (~91%) of Ir(III) was achieved at 0.10 mol L^{-1} H_2SO_4 and decreased thereafter, attaining a minimum value (~20%) at 6.0 mol L^{-1} H_2SO_4. The extraction of Ir(III) from nitrate medium varied between 32% and 54% in the investigated range of acid molarity. Rh(III) shows low or negligible extraction in all the three mineral acids. The extraction of Ru(III) remains more or less constant and ranges between 18% and 36% in all the three mineral acids in the investigated range of acid molarity. Detailed studies were conducted on platinum and iridium at 1.0 mol L^{-1} HCl and 2.0 mol L^{-1} H_2SO_4, respectively.

Effect of equilibration time

The equilibration time for Pt(IV) and Ir(III) was varied from one minute to thirty minutes (figure 4.4). The results indicate that the equilibrium for both the metal ions was achieved in about four minutes and prolonged shaking had no adverse effect on the partition of both the metal ions. In all the studies six minutes shaking time was observed.

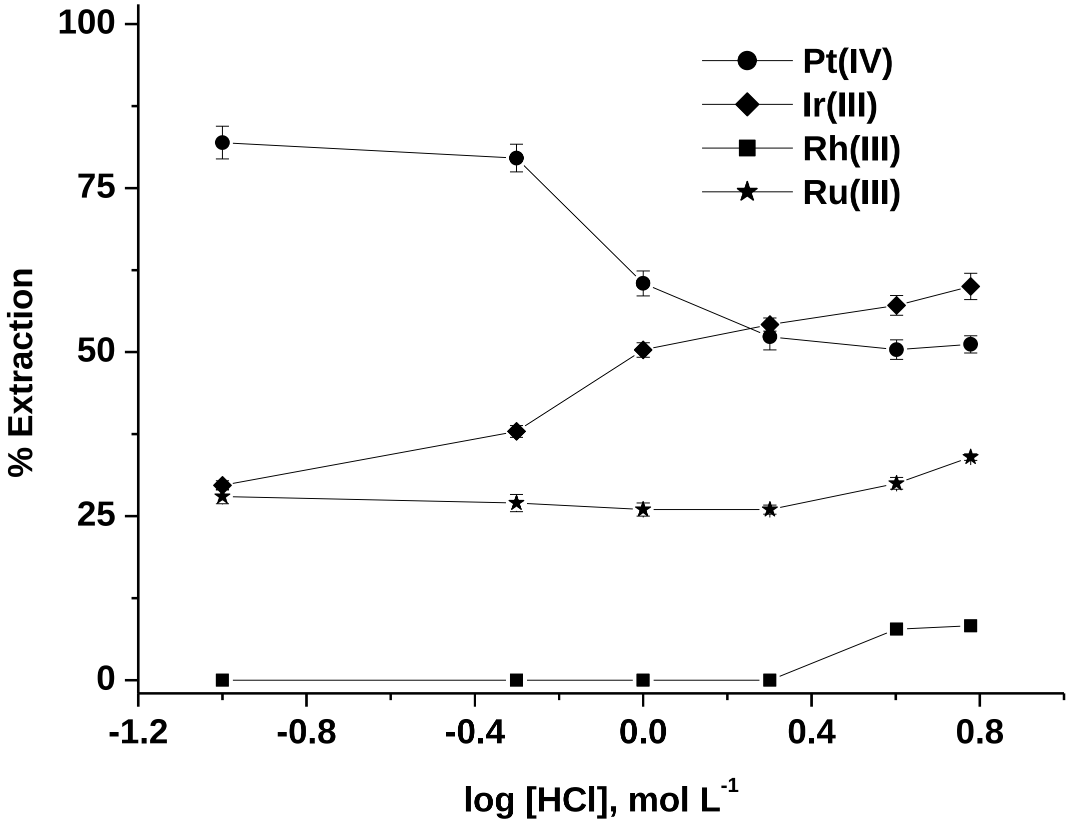


FIGURE 4.1: Effect of concentration of hydrochloric acid on the extraction of Pt(IV), Ir(III), Rh(III) and Ru(III)

Conditions

[Cyanex 471X] = 0.10 mol L^{-1}

[Metal ion] = 5 x 10^{-4} mol L^{-1}

[HCl] = 0.1 - 6.0 mol L^{-1}

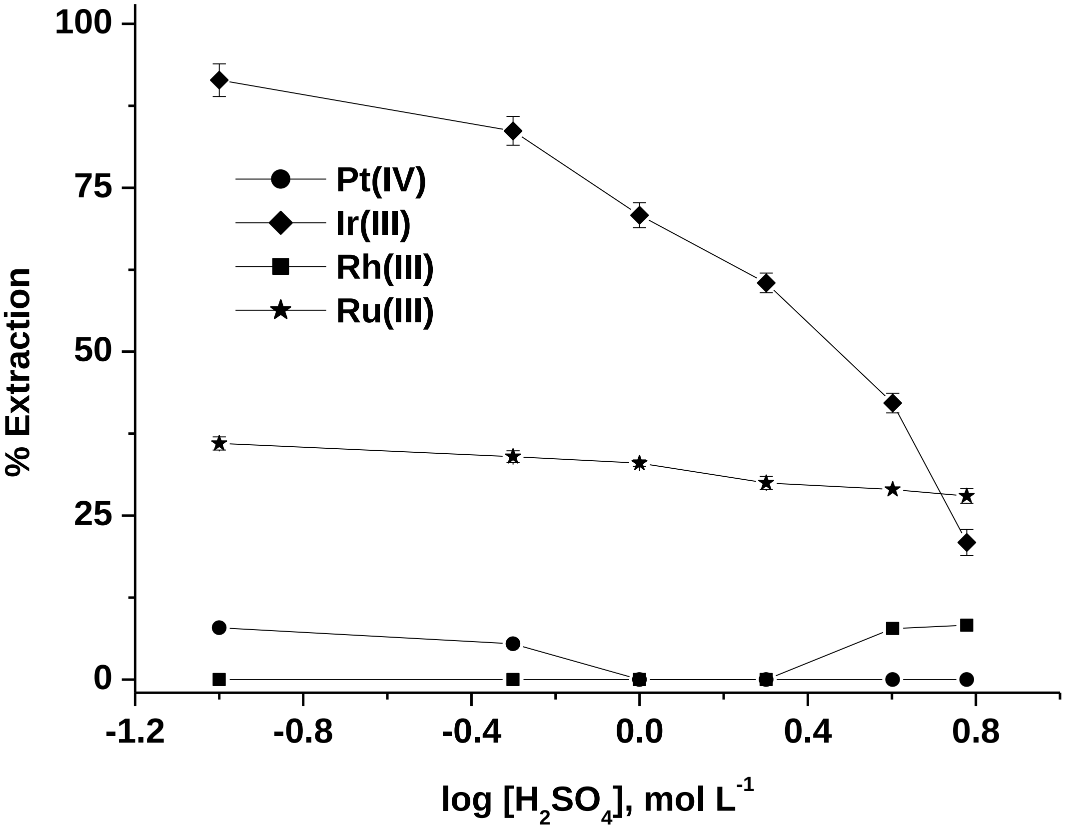


FIGURE 4.2: Effect of concentration of sulphuric acid on the extraction of Pt(IV), Ir(III), Rh(III) and Ru(III)

Conditions

[Cyanex 471X] = 0.10 mol L^{-1}

[Metal ion] = 5 x 10^{-4} mol L^{-1}

[H_2SO_4] = 0.1 - 6.0 mol L^{-1}

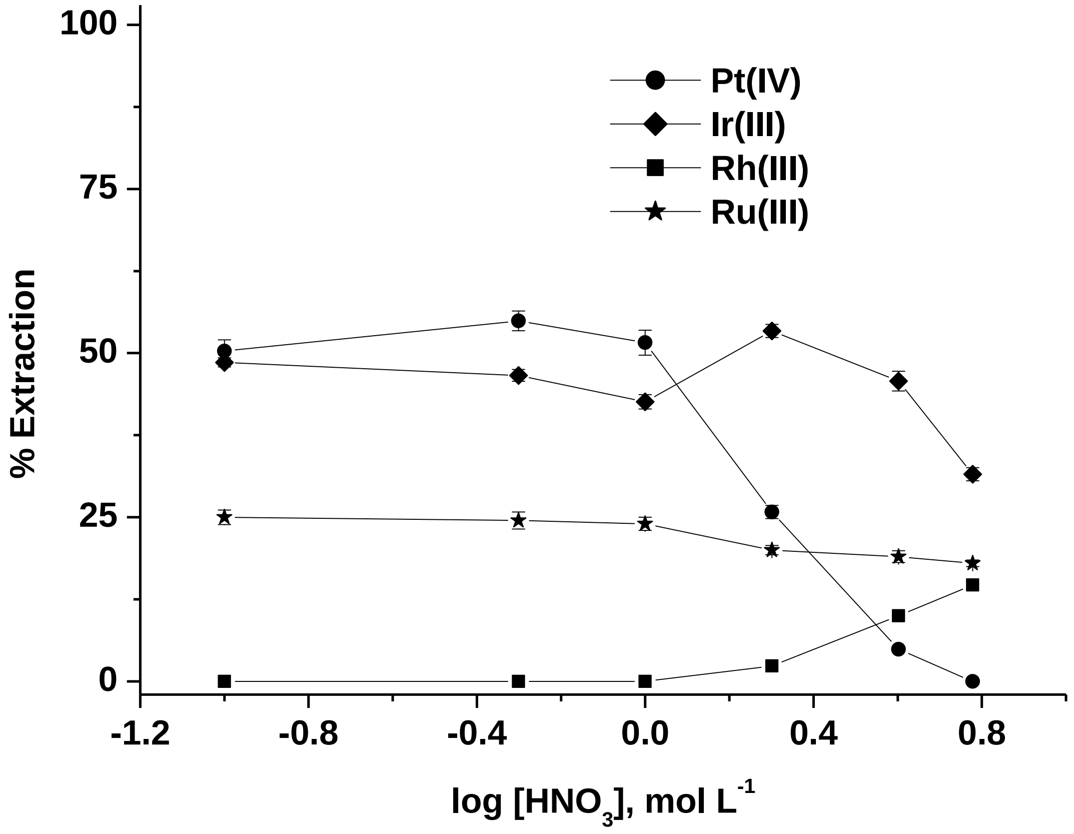


FIGURE 4.3: Effect of concentration of nitric acid on the extraction of Pt(IV), Ir(III), Rh(III) and Ru(III)

Conditions

[Cyanex 471X] = 0.10 mol L^{-1}

[Metal ion] = 5 x 10^{-4} mol L^{-1}

[HNO_3] = 0.1 - 6.0 mol L^{-1}

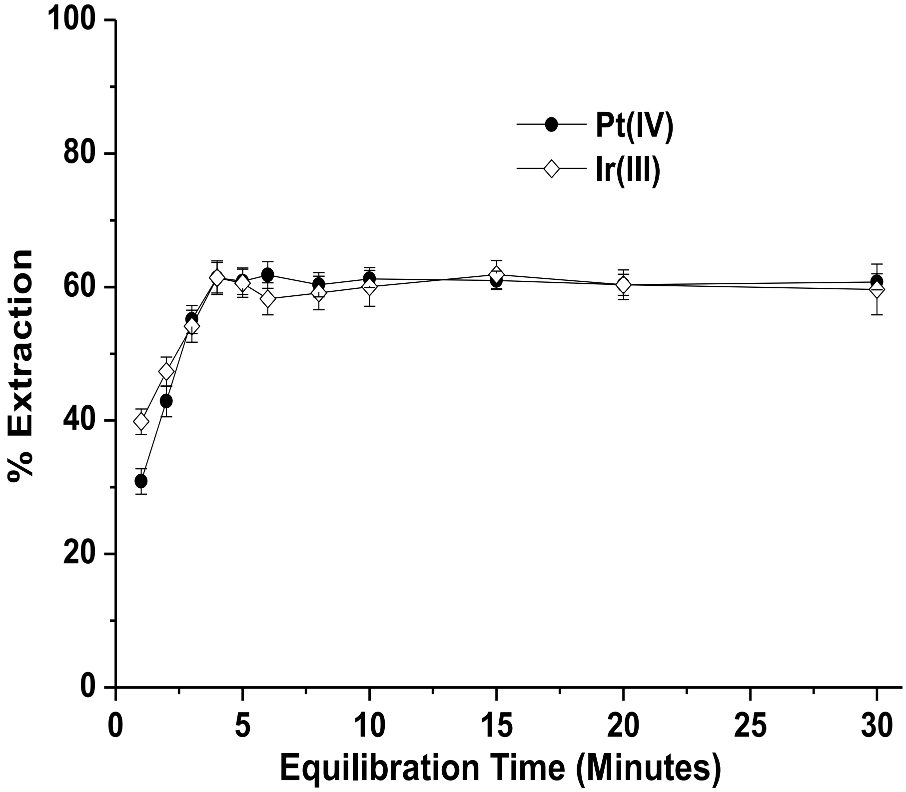


FIGURE 4.4: Effect of equilibration time on the extraction of Pt(IV) and Ir(III)

Conditions

[Cyanex 471X] = 0.10 mol L^{-1}

[Metal ion] = 5 x 10^{-4} mol L^{-1}

[HCl] = 1.0 mol L^{-1} (Pt(IV))

[H_2SO_4] = 2.0 mol L^{-1} (Ir(III))

Effect of temperature

The effect of temperature in the range of 10 – 50 ^{o}C on the extraction of Pt(IV) and Ir(III) has been investigated at 1.0 mol L^{-1} HCl and 2.0 mol L^{-1} H_2SO_4, respectively, using 0.10 mol L^{-1} Cyanex 471X (figure 4.5). The results indicate the process to be exothermic in the case of Pt(IV) and endothermic for Ir(III). The plots between the reciprocal of absolute temperature and log K gave straight lines with a positive slope value of 0.49 for Pt(IV) and negative slope value of -0.60 for Ir(III). The values of ΔH as calculated from the Van't Hoff equation are -5.25 and 19.51 kJ/mol for Pt(IV) and Ir(III), respectively. All further studies were carried out at room temperature (25 ± 3 ^{o}C).

Effect of concentration of extractant

The effect of varying Cyanex 471X concentration (0.005 to 0.5 mol L^{-1}) on the distribution of Pt(IV) and Ir(III) was investigated at 1.0 mol L^{-1} HCl and 2.0 mol L^{-1} H_2SO_4, respectively. With the increasing extractant concentration an increase in the extraction of both the metal ions was observed. Log-log plots (figure 4.6) between extractant concentration and distribution ratio gave straight lines with slope values around one and two for Pt(IV) and Ir(III), respectively. The above findings indicate the involvement of one and two molecule of Cyanex 471X in the formation of the extracting species of Pt(IV) and Ir(III), respectively. Similar metal:ligand ratio for Pt(IV) and Cyanex 471X in bromide medium has been reported earlier (23).

Effect of the nature of diluent

A number of solvents namely nitrobenzene, cyclohexane, chloroform, toluene, xylene, kerosene (160 – 200 ^{o}C) and n-hexane were employed to discern the effect of varying nature of the organic diluents on the extraction of Pt(IV) and Ir(III). The results are given in table 4.1. No correlation between the nature of organic diluents and percent extraction was observed. In all further studies toluene was used as a diluent.

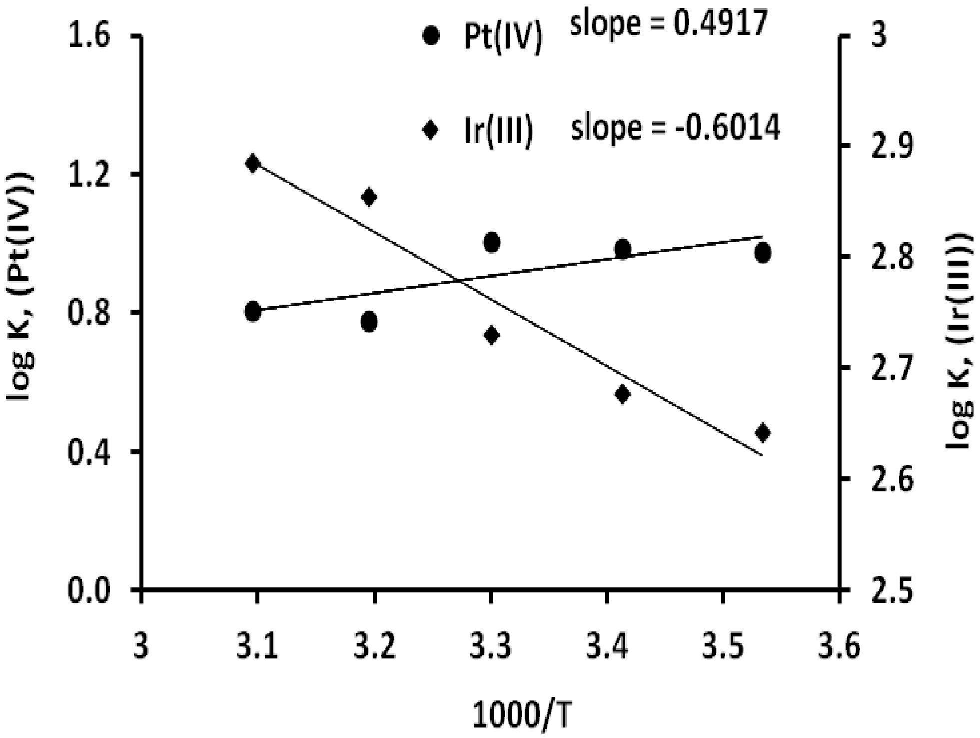


FIGURE 4.5: Effect of temperature on the extraction of Pt(IV) and Ir(III)

Conditions

[Cyanex 471X] = 0.10 mol L^{-1}

[Metal ion] = 5 x 10^{-4} mol L^{-1}

[HCl] = 1.0 mol L^{-1} (Pt(IV))

[H_2SO_4] = 2.0 mol L^{-1} (Ir(III))

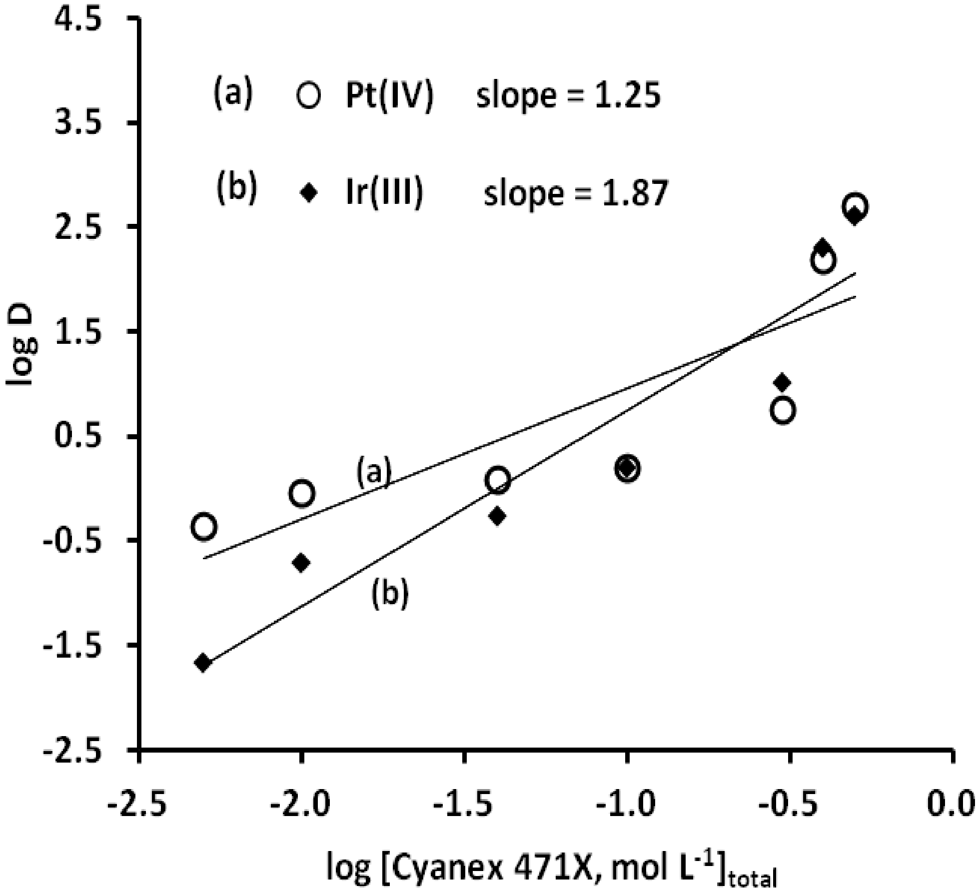


FIGURE 4.6: Effect of extractant concentration on the extraction of Pt(IV) and Ir(III)

Conditions

[Cyanex 471X] = 0.10 mol L^{-1}

[Metal ion] = 5 x 10^{-4} mol L^{-1}

[HCl] = 1.0 mol L^{-1} (Pt(IV))

[H_2SO_4] = 2.0 mol L^{-1} (Ir(III))

Table 4.1. Effect of the nature of various diluents on the extraction of Pt(IV) and Ir(III).

Diluent	Dielectric constant	Percent extraction	
		Pt(IV)	Ir(III)
Nitrobenzene	35.70	52.87	57.41
Cyclohexane	18.3	52.77	58.17
Chloroform	4.81	53.91	56.15
Toluene	2.44	54.62	60.48
Xylene	2.20	51.11	62.74
Kerosene	2.02	49.95	58.86
n-hexane	1.891	52.18	57.61

Conditions

[Cyanex 471X] = 0.10 mol L^{-1}

[Metal ion] = 5 x 10^{-4} mol L^{-1}

[HCl] = 1.0 mol L^{-1} (Pt(IV))

[H_2SO_4] = 2.0 mol L^{-1} (Ir(III))

Loading capacity

The loading capacity of Cyanex 471X diluted with toluene was determined by shaking an aqueous solution of Pt(IV)/Ir(III) in 0.10 mol L^{-1} HCl/H_2SO_4 with equal volume of 0.10 mol L^{-1} Cyanex 471X. After equilibrium, the two phases were separated and the aqueous phase was analysed for Pt(IV)/Ir(III) content. The organic phase was equilibrated again with the fresh aqueous phase for the extraction of Pt(IV)/Ir(III). This procedure was repeated till no further extraction of Pt(IV)/Ir(III) was observed in the organic phase. The amount of metal transferred into the organic phase in each contact was calculated by the difference in metal ion concentration in the aqueous phase before and after extraction for each contact. The cumulative increase in the concentration of metal in the organic phase after each stage of contact was thus obtained. The plot of cumulative $[\text{metal}]_{org}$ against contact number is given in figure 4.7. The results reveal that the complete loading of the extractant with respect to Pt(IV) and Ir(III) is achieved after nineteenth and twelfth stages of contact, respectively. The results of loading reveal that the maximum loading obtained is 62 mM Pt(IV) per 0.10 M extractant and 46 mM Ir(III) per 0.10 M extractant.

Hydrolytic stability and regeneration power of Cyanex 471X

The stability and regeneration capacity of Cyanex 471X were assessed for its potential as a commercial extractant. A 0.10 mol L^{-1} toluene solution of Cyanex 471X was kept in contact with 6.0 mol L^{-1} HCl/H_2SO_4 for 50 days with intermittent shaking. A known aliquot of the extractant solution was removed periodically after five days and employed for the extraction of Pt(IV)/Ir(III) at 0.10 mol L^{-1} HCl/H_2SO_4. An insignificant change (2-3%) in the percent extraction of Pt(IV) and Ir(III) (figure 4.8) was observed after a contact period of 50 and 40 days, respectively.

The studies on the successive extraction (Pt(IV) from 1.0 mol L^{-1} HCl and Ir(III) from 2.0 mol L^{-1} H_2SO_4) and stripping (Pt(IV) with 6.0 mol L^{-1} H_2SO_4 and Ir(III) with acidic solution of 0.10 mol L^{-1} thiourea) cycle for Pt(IV) and Ir(III) revealed negligible change (2-3%) in the percent extraction/stripping of Pt(IV)/Ir(III) up to six and eleven cycles, respectively (figure 4.9).

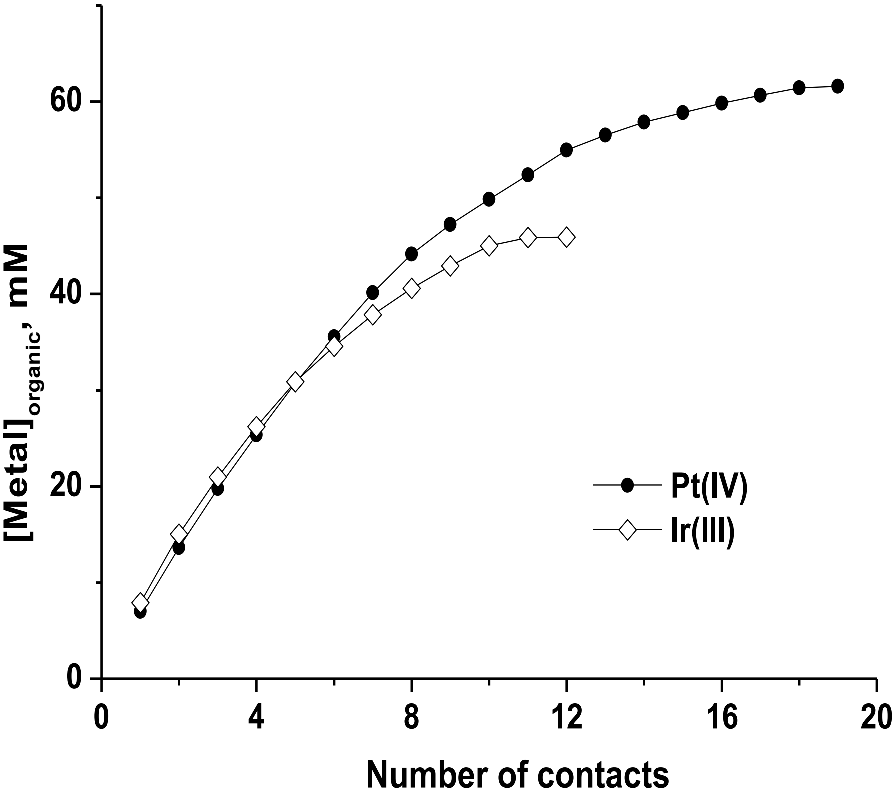


FIGURE 4.7: Loading capacity of Cyanex 471X towards Pt(IV) and Ir(III)

Conditions

[Cyanex 471X] = 0.10 mol L^{-1}

[Metal ion] = 5 x 10^{-4} mol L^{-1}

[HCl] = 1.0 mol L^{-1} (Pt(IV))

[H_2SO_4] = 2.0 mol L^{-1} (Ir(III))

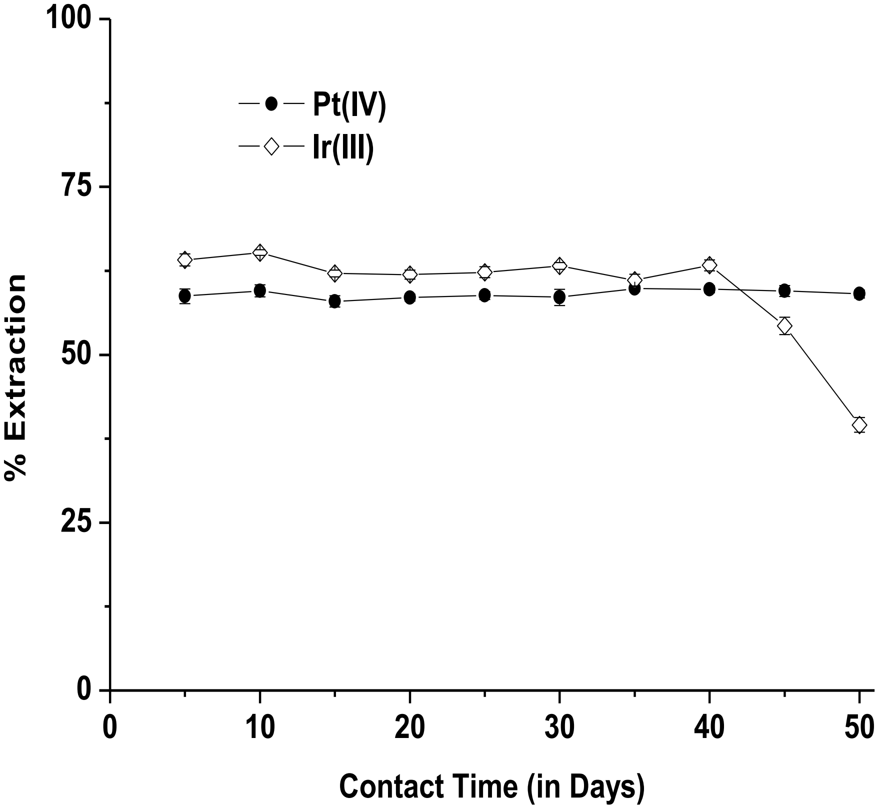


FIGURE 4.8: Variation in the extraction of Pt(IV)/Ir(III) using Cyanex 471X solution kept in contact with 6.0 mol L^{-1} HCl/H_2SO_4

Conditions

[Cyanex 471X] = 0.10 mol L^{-1}

[Metal ion] = 5 x 10^{-4} mol L^{-1}

[HCl] = 6.0 mol L^{-1} (Pt(IV))

[H_2SO_4] = 6.0 mol L^{-1} (Ir(III))

Table 4.2. Efficiency of various stripping reagents for Pt(IV) and Ir(III).

Strippant used	% Stripping	
	Pt(IV)	Ir(III)
5 mol L^{-1} Citric acid	1.8	7.16
0.1 mol L^{-1} EDTA	0	11.15
6 mol L^{-1} H_2SO_4	100	45.06
0.1 mol L^{-1} Thiourea	14.62	0
0.4 mol L^{-1} Malonic acid	50.98	33.67
0.1 mol L^{-1} Thiourea + 0.1 mol L^{-1} HNO_3	20.11	36.92
0.1 mol L^{-1} Thiourea + 1 mol L^{-1} $HClO_4$	11.26	60.54
0.1 mol L^{-1} Thiourea + 0.1 mol L^{-1} HCl	25.81	100

Conditions:

[Cyanex 471X] = 0.1 mol L^{-1}

[Metal ion] = 5 x 10^{-4} mol L^{-1}

[HCl] = 1.0 mol L^{-1} for Pt(IV)

[H_2SO_4] = 2.0 mol L^{-1} for Ir(III)

Organic:aqueous = 1:1

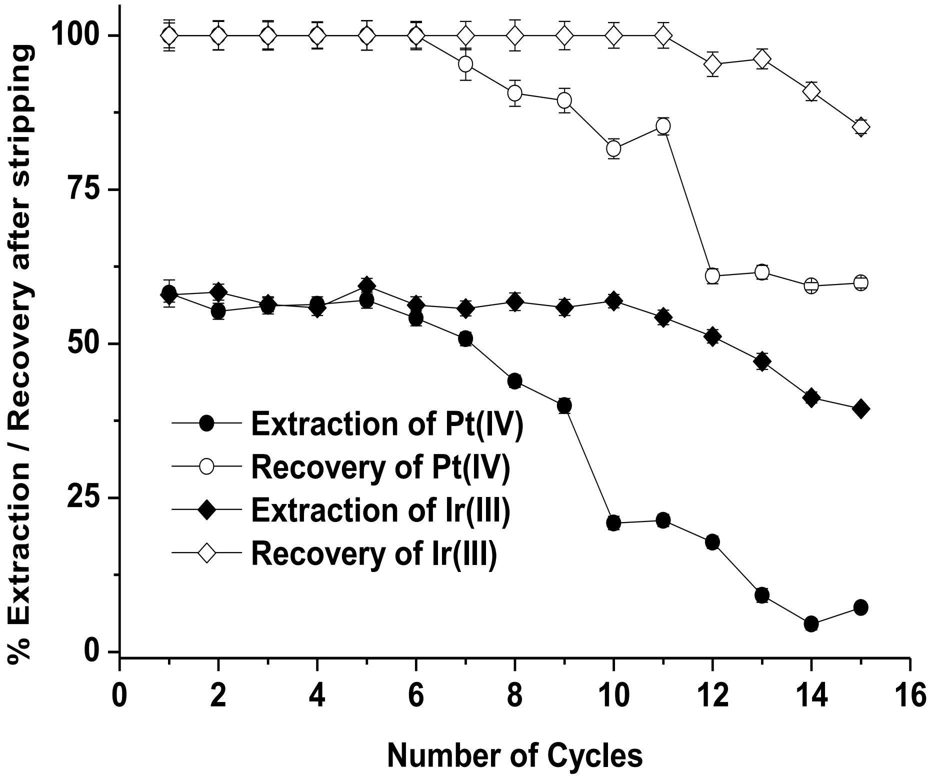


FIGURE 4.9: Variation in the extraction / recovery of Pt(IV)/Ir(III) in successive

Conditions

[Cyanex 471X] = 0.10 mol L^{-1}

[Metal ion] = 5 x 10^{-4} mol L^{-1}

[HCl] = 1.0 mol L^{-1} (Pt(IV))

[H_2SO_4] = 2.0 mol L^{-1} (Ir(III))

[Strippant] = 6.0 mol L^{-1} H_2SO_4 (for Pt(IV))

= acidic 0.10 mol L^{-1} thiourea (for Ir(III))

Stripping

Various stripping reagents were tried for the back extraction of Pt(IV) and Ir(III) from the loaded organic phase. The results are given in table 4.2. The results suggest that 6.0 mol L^{-1} H_2SO_4 was suitable for the quantitative stripping of Pt(IV) whereas, acidic solution of 0.10 mol L^{-1} thiourea was found effective for the stripping of Ir(III). The organic phase after stripping was regenerated by washing with water until the washings were nearly neutral.

Extraction behaviour of associated metal ions

Pt(IV) and Ir(III) show 80-90% extraction from HCl and H_2SO_4 medium, respectively. Therefore the binary separations involving platinum group metals and associated metal ions were carried out from HCl and H_2SO_4 media.

HCl

The extraction behaviour of associated metal ions, namely Au(III), Cr(III), Fe(III), Cu(II), Ni(II), Co(II) and Fe(II) from hydrochloric acid medium is shown in figure 4.10. Au(III) is extracted quantitatively in the investigated range of acid molarity whereas, Cr(III), Cu(II), Ni(II) and Fe(II) show poor extraction ($\leq$11%). The extraction of Fe(III) ranges between 18% and 51% in the studied range of acidity. At low acidity Co(II) shows negligible extraction which gradually increases to around 20% at 6.0 mol L^{-1} HCl.

H_2SO_4

The extraction behavior of associated metal ions, namely Au(III), Cr(III), Fe(III), Cu(II), Ni(II), Co(II), Fe(II) and Ag(I), from H_2SO_4 medium is shown in figure 4.11. The extraction of Fe(II), Cu(II) and Co(II) is poor ($\leq$10%), whereas Au(III) and Ag(I) show quantitative extraction in the investigated range of acid molarity. A maximum extraction of Fe(III) (~40%) is achieved at 0.10 mol L^{-1} H_2SO_4 which decreases slightly with the increasing acid molarity. Cr(III) and Ni(II) show negligible extraction at low acid molarity which increases to around 20% at high acidity.

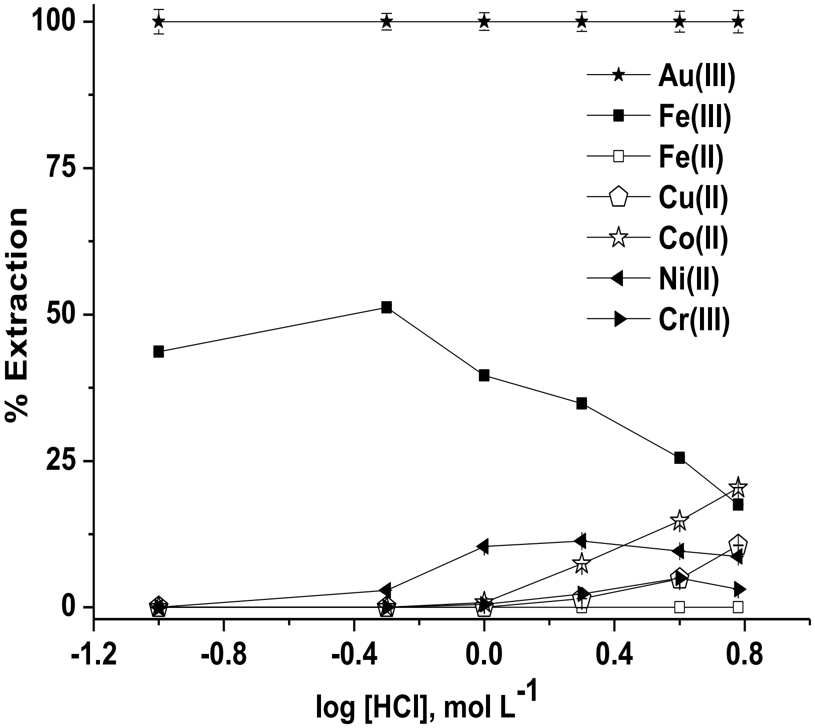


FIGURE 4.10: Effect of concentration of hydrochloric acid on the extraction of associated metal ions

Conditions

[Cyanex 471X] = 0.10 mol L^{-1}

[Metal ion] = 5 x 10^{-4} mol L^{-1}

[HCl] = 0.1 - 6.0 mol L^{-1}

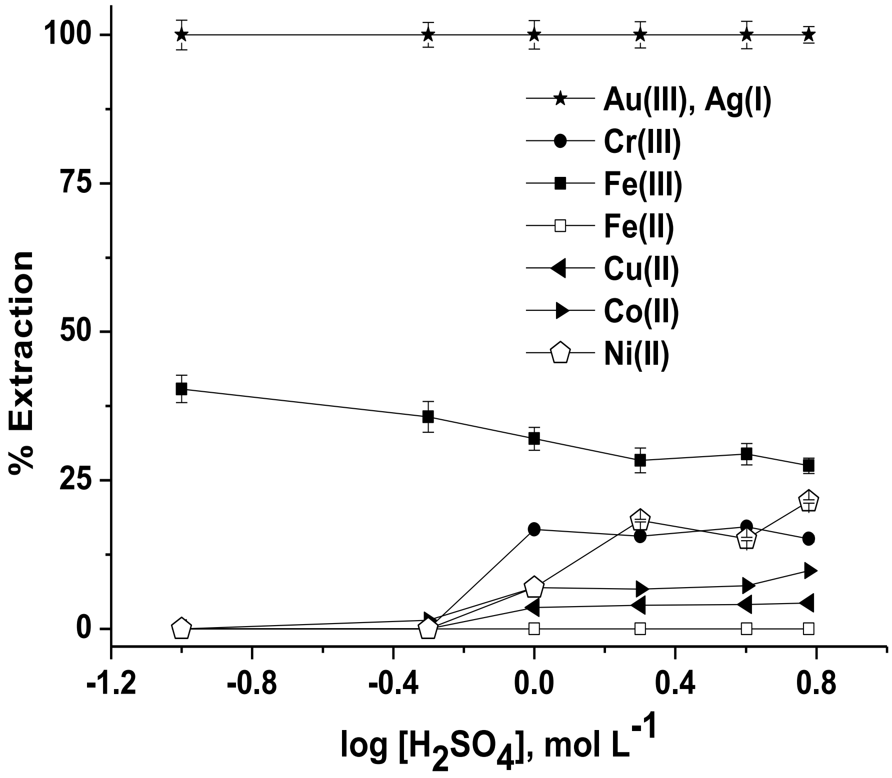


FIGURE 4.11: Effect of concentration of sulphuric acid on the extraction of associated metal ions

Conditions

[Cyanex 471X] = 0.10 mol L^{-1}

[Metal ion] = 5 x 10^{-4} mol L^{-1}

[H_2SO_4] = 0.1 - 6.0 mol L^{-1}

Separations

The partition data obtained provide conditions for the separation of Pt(IV) and Ir(III) from each other and from the associated metal ions. A number of binary separations of analytical importance involving Pt(IV) and Ir(III) were carried out. The results indicating the conditions for the separations, percentage recovery and separation factor of the metal ions are tabulated in tables 4.3 and 4.4.

Binary separations

Pt(IV)

All the binary separations of Pt(IV) were carried out at 0.10 mol L^{-1} HCl where maximum value of separation factor is achieved. Moreover, the aqueous and organic phases were equilibrated thrice in order to achieve quantitative transfer of Pt(IV) into the organic phase. Pt(IV) is separated from Rh(III)/Cr(III)/Cu(II)/Ni(II)/Co(II) by extracting the former using 0.10 mol L^{-1} Cyanex 471X leaving the other metal ions in the aqueous phase. As Fe(III) is partially co-extracted with Pt(IV), Fe(III) was first reduced to Fe(II) using ascorbic acid (0.05 mol L^{-1}) followed by the extraction of Pt(IV) at 0.10 mol L^{-1} HCl. This resulted in to quantitative extraction of Pt(IV) leaving Fe(II) in the raffinate. Pt(IV) was then recovered by washing the organic phase with 6.0 mol L^{-1} H_2SO_4. The Pt(IV)-Au(III) separation was carried out by equilibrating the aqueous layer with 0.10 mol L^{-1} Cyanex 471X. This step transferred both the metal ions to the organic phase. Au(III) was then selectively stripped from the loaded organic phase employing water followed by the scrubbing of Pt(IV) using 6.0 mol L^{-1} H_2SO_4.

Ir(III)

The separation of Ir(III) from the associated metal ions has been achieved at 0.10 mol L^{-1} H_2SO_4 where maximum value of separation factor is obtained. The equilibration was carried out thrice to attain quantitative extraction of Ir(III). At this acidity Ir(III) is extracted leaving behind Pt(IV)/Rh(III)/Cr(III)/Cu(II)/Ni(II)/Co(II) in the aqueous phase. The Fe(III) was reduced to Fe(II) prior to separation which resulted in selective extraction of Ir(III) leaving Fe(II) in the raffinate. In all the above cases Ir(III) was recovered from the loaded

Table 4.3. Binary separations of Pt(IV) using 0.10 mol L^{-1} Cyanex 471X

Metal ions separated*	Molar ratio	Acid molarity (mol L^{-1}), HCl	Metal ion remaining in the aqueous phase (%)	Metal ion transferred into the organic phase (%)	Recovery of metal ion from the organic phase (%)[a]	Separation factor, β (based on single extraction)
Pt(IV):Rh(III)	1:10 10:1	0.1	100 ± 0.7, Rh 100 ± 0.6, Rh	99 ± 1.0, Pt 99 ± 0.9, Pt	98 ± 1.2, Pt 99 ± 1.1, Pt	4.5×10^4 4.7×10^4
Pt(IV):Au(III)	1:10	0.1	- -	99 ± 1.1, Pt 100 ± 1.0, Au	99 ± 1.1, Pt 100 ± 1.0, Au	
	10:1		- -	99 ± 1.2, Pt 100 ± 1.0, Au	98 ± 1.2, Pt 99 ± 1.0, Au	
Pt(IV):Cr(III)	1:10 10:1	0.1	99 ± 1.0, Cr 99 ± 1.1, Cr	98 ± 1.1, Pt 99 ± 1.3, Pt	98 ± 1.0, Pt 99 ± 1.1, Pt	8.03×10^3 8.05×10^3
Pt(IV):Cu(II)	1:10 10:1	0.1	99 ± 1.1, Cu 100 ± 0.5, Cu	99 ± 0.9, Pt 99 ± 1.0, Pt	100 ± 1.1, Pt 100 ± 1.0, Pt	8.34×10^3 5.0×10^4
Pt(IV):Ni(II)	1:10 10:1	0.1	99 ± 1.1, Ni 99 ± 1.0, Ni	97 ± 1.0, Pt 98 ± 0.9, Pt	98 ± 1.0, Pt 100 ± 0.9, Pt	8.14×10^3 8.11×10^3
Pt(IV):Co(II)	1:10 10:1	0.1	100 ± 0.6, Co 99 ± 1.1, Co	98 ± 1.0, Pt 98 ± 1.1, Pt	97 ± 0.9, Pt 98 ± 1.0, Pt	4.9×10^4 8.25×10^3
Pt(IV):Fe(II)	1:10 10:1	0.1	100 ± 0.7, Fe 100 ± 0.6, Fe	99 ± 1.0, Pt 99 ± 0.9, Pt	98 ± 1.2, Pt 99 ± 1.1, Pt	4.5×10^4 4.7×10^4

Note: '±' refers to the standard deviation

*The aqueous phase was equilibrated thrice with the equal volume of organic phase.

[a] Pt(IV) recovered using 6.0 mol L^{-1} H_2SO_4, Au(III) using water and Ag(I) using 0.01 mol L^{-1} thiourea.

organic phase by washing with acidic 0.10 mol L^{-1} thiourea. For Ir(III)-Au(III) separation, aqueous phase was equilibrated with 0.10 mol L^{-1} Cyanex 471X. This step transferred both the metal ions to the organic phase. Au(III) was stripped first by washing the organic phase with water followed by the recovery of Ir(III) with acidic 0.10 mol L^{-1} thiourea. For achieving Ir(III)-Ag(I) separation both the metal ions were first extracted by equilibrating the aqueous phase with 0.10 mol L^{-1} Cyanex 471X. Ag(I) was then selectively stripped with 0.01 mol L^{-1} thiourea followed by the stripping of Ir(III) with acidic 0.10 mol L^{-1} thiourea.

The above binary separations attained using Cyanex 471X provide a database for the purification of Pt(IV)/Ir(III) and developing procedures for the recovery of Pt(IV)/Ir(III) from different matrices.

Recovery of Pt(IV), Ir(III) and Rh(III)

As a first step the conditions of proposed binary separations were fused together to design procedures for the separation and recovery of Pt(IV)/Ir(III)/Rh(III) from synthetic solution using Cyanex 471X (flowsheet 4.1).

From synthetic mixture

Based on the extraction data a scheme (flowsheet 4.1) was designed to recover Pt(IV), Ir(III), Rh(III), Au(III) and Ag(I) from synthetic mixture. Different steps of the scheme are detailed below.

50 mL of aqueous solution [A1] containing equimolar concentrations of platinum(IV), iridium(III), rhodium(III), gold(III) and silver(I) at 0.10 mol L^{-1} H_2SO_4 was equilibrated thrice with equal volume of 0.10 mol L^{-1} Cyanex 471X. Ir(III), Au(III) and Ag(I) were quantitatively extracted while Pt(IV) and Rh(III) remained in the aqueous phase [A2] which is evaporated to near dryness. The residue was mixed with 7 mL of HNO_3 (2 mol L^{-1}) and again evaporated to near dryness. The procedure was repeated thrice. The residue was dissolved in HCl adjusting the final acidity to 0.10 mol L^{-1} HCl and final volume to 50 mL. The resulting solution was then equilibrated thrice with equal volume of 0.10 mol L^{-1} Cyanex 471X which extracted Pt(IV) leaving Rh(III) in the aqueous phase [A3]. The extracted Pt(IV) was then recovered with 6.0 mol L^{-1} H_2SO_4 [A4]. The organic

Table 4.4. Binary separations of Ir(III) using 0.10 mol L^{-1} Cyanex 471X

Metal ions separated*	Molar ratio	Acid molarity (mol L^{-1}), H_2SO_4	Metal ion remaining in the aqueous phase (%)	Metal ion transferred into the organic phase (%)	Recovery of metal ion from the organic phase (%)[a]	Separation factor, β (based on single extraction)
Ir(III):Pt(IV)	1:10	0.1	99 ± 1.0, Pt	99 ± 0.7, Ir	98 ± 1.1, Ir	2.2 x 10^3
	10:1		100 ± 0.4, Pt	99 ± 0.9, Ir	99 ± 1.0, Ir	1.2 x 10^4
Ir(III):Rh(III)	1:10	0.1	99 ± 1.0, Rh	99 ± 1.0, Ir	100 ± 0.6, Ir	2.1 x 10^3
	10:1		99 ± 1.0, Rh	98 ± 1.1, Ir	99 ± 1.1, Ir	1.1 x 10^4
Ir(III):Au(III)	1:10	0.1	-	100 ± 1.0, Ir	99 ± 0.9, Ir	
			-	97 ± 1.0, Au	100 ± 0.8, Au	
	10:1		-	98 ± 0.9, Ir	98 ± 0.9, Ir	
			-	99 ± 1.0, Au	100 ± 0.7, Au	
Ir(III):Cr(III)	1:10	0.1	99 ± 1.0, Cr	97 ± 1.1, Ir	98 ± 0.9, Ir	$2.0\text{x}10^3$
	10:1		99 ± 1.0, Cr	98 ± 1.2, Ir	99 ± 1.0, Ir	$2.1\text{x}10^3$
Ir(III):Cu(II)	1:10	0.1	99 ± 1.0, Cu	99 ± 0.8, Ir	99 ± 1.0, Ir	$2.0\text{x}10^3$
	10:1		99 ± 1.0, Cu	97 ± 0.7, Ir	97 ± 1.1, Ir	$2.0\text{x}10^3$
Ir(III):Ni(II)	1:10	0.1	100 ± 0.5, Ni	98 ± 1.1, Ir	98 ± 0.9, Ir	$11.3\text{x}10^4$
	10:1		99 ± 0.8, Ni	97 ± 1.0, Ir	99 ± 1.0, Ir	$2.0\text{x}10^3$
Ir(III):Co(II)	1:10	0.1	99 ± 0.8, Co	99 ± 0.9, Ir	99 ± 1.1, Ir	$2.0\text{x}10^3$
	10:1		99 ± 1.1, Co	98 ± 0.7, Ir	98 ± 0.8, Ir	$2.1\text{x}10^3$
Ir(III):Fe(II)	1:10	0.1	100 ± 0.5, Fe	99 ± 0.9, Ir	98 ± 1.1, Ir	10.810^4
	10:1		100 ± 0.8, Fe	99 ± 1.1, Ir	99 ± 1.3, Ir	$9.9\text{x}10^4$
Ir(III):Ag(I)	1:10	0.1	-	100 ± 1.0, Ir	99 ± 0.9, Ir	
	10:1		-	98 ± 1.0, Ag	99 ± 0.8, Ag	
			-	97 ± 0.9, Ir	99 ± 0.9, Ir	
			-	99 ± 1.0, Ag	97 ± 0.7, Ag	

Note: '±' refers to the standard deviation

*The aqueous phase was equilibrated thrice with the equal volume of organic phase.

[a] Ir(III) recovered using acidic 0.1 mol L^{-1} thiourea, Au(III) using water and Ag(I) using 0.01 mol L^{-1} thiourea

phase containing Ir(III), Au(III) and Ag(I) was scrubbed with water to recover Au(III) [A5] and the co-extracted Ag(I) was stripped using 0.01 mol L^{-1} thiourea [A6]. Finally Ir(III) was recovered employing acidic 0.10 mol L^{-1} thiourea [A7]. The concentration of the metal ions in the initial and the recovered solutions are given in table 4.5. The flowsheet 4.1 can be used to recover platinum, iridium, rhodium, gold and silver from real samples.

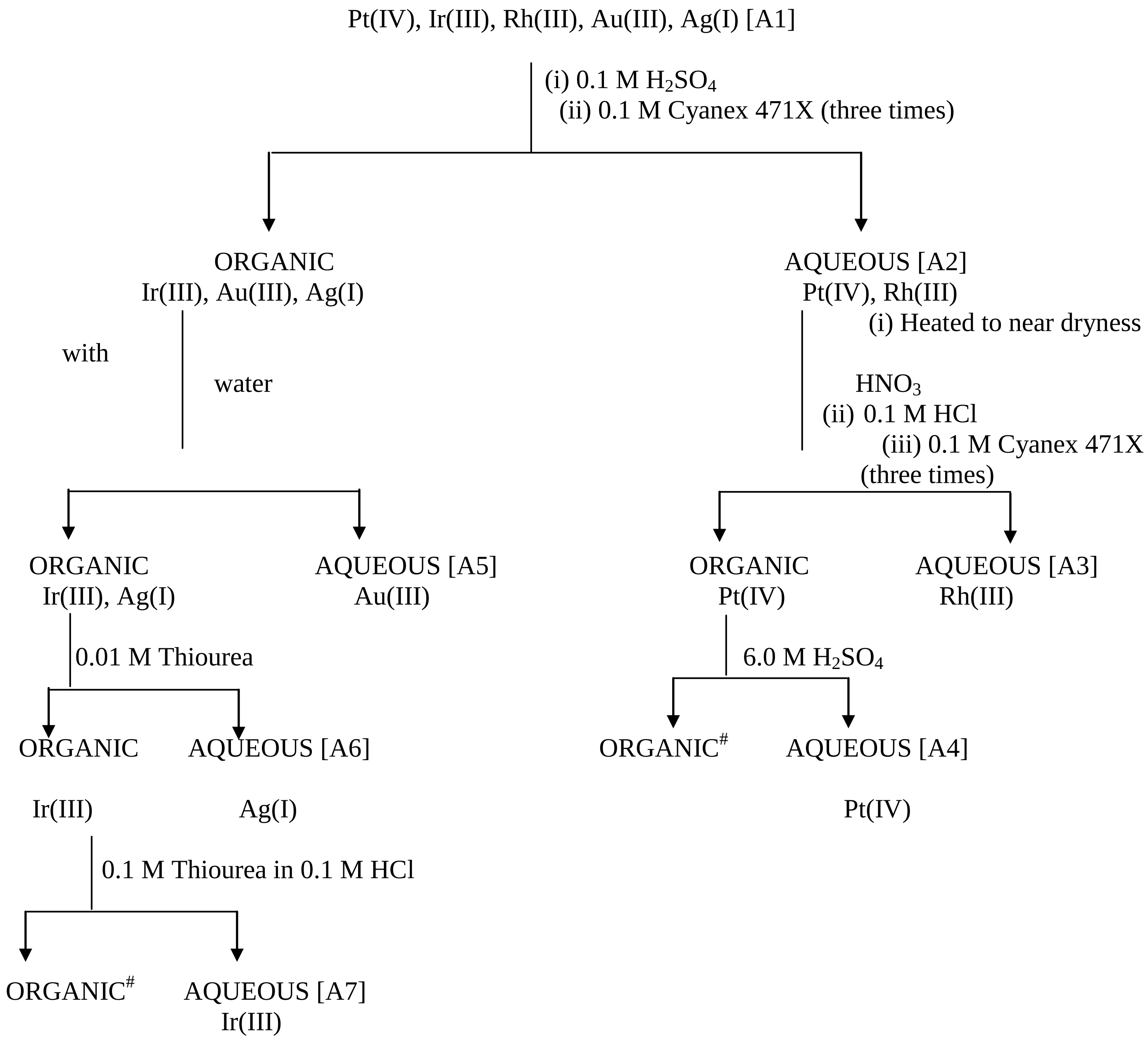
From Pt-Rh thermocouple wire

The results of separation studies were successfully applied for the recovery of platinum and rhodium from Pt-Rh thermocouple wire. The digested solution of Pt-Rh thermocouple [T1] was used for the recovery of platinum and rhodium (flowsheet 4.2). The solution [T1] was contacted thrice with equal volume of 0.1 mol L^{-1} Cyanex 471X. Pt(IV) was quantitatively extracted while Rh(III) remained in the aqueous phase [T2]. The extracted Pt(IV) was scrubbed employing 6.0 mol L^{-1} H_2SO_4 [T3]. The composition of the solutions [T1], [T2] and [T3] are given in table 4.6.

The investigations conducted herein bring forth the potential of Cyanex 471X for the separation and recovery of Pt(IV), Ir(III) and Rh(III). A quantitative extraction of Pt(IV) and Ir(III) was achieved in HCl and H_2SO_4 media, respectively. Both the metal ions are conveniently separated from associated metal ions by selective extraction/stripping.

The results embodied in this chapter have been communicated in the form of one paper in “Separation and Purification Technology”.

Flowsheet 4.1: Recovery of PGMs from synthetic mixture using Cyanex 471X



organic phase can be regenerated by washing with water.

Table 4.5. Recovery of Pt(IV), Ir(III), Rh(III), Au(III) and Ag(I) from a synthetic mixture using 0.1 mol L^{-1} Cyanex 471X

Metal ions	Composition of initial solution [A1] (mg/l)	Composition of solution [A3] (mg/l)	Composition of solution [A4] (mg/l)	Composition of solution [A5] (mg/l)	Composition of solution [A6] (mg/l)	Composition of solution [A7] (mg/l)	Recovery (%)	Purity (%)
Pt	102.7 ± 1.8	<0.05	102.2 ± 1.6	<0.05	<0.05	<0.05	99.5	99.75
Ir	103.1 ± 2.0	<0.05	<0.05	<0.05	<0.05	103.0	99.9	99.76
Rh	51.8 ± 1.1	52.0 ± 1.4	<0.1	<0.1	<0.1	<0.1	100	99.62
Au	98.5 ± 1.7	<0.05	<0.05	98.3 ± 2.0	<0.05	<0.05	99.8	99.74
Ag	53.7 ± 1.0	<0.05	<0.05	<0.05	54.1 ± 0.8	<0.05	100	99.54

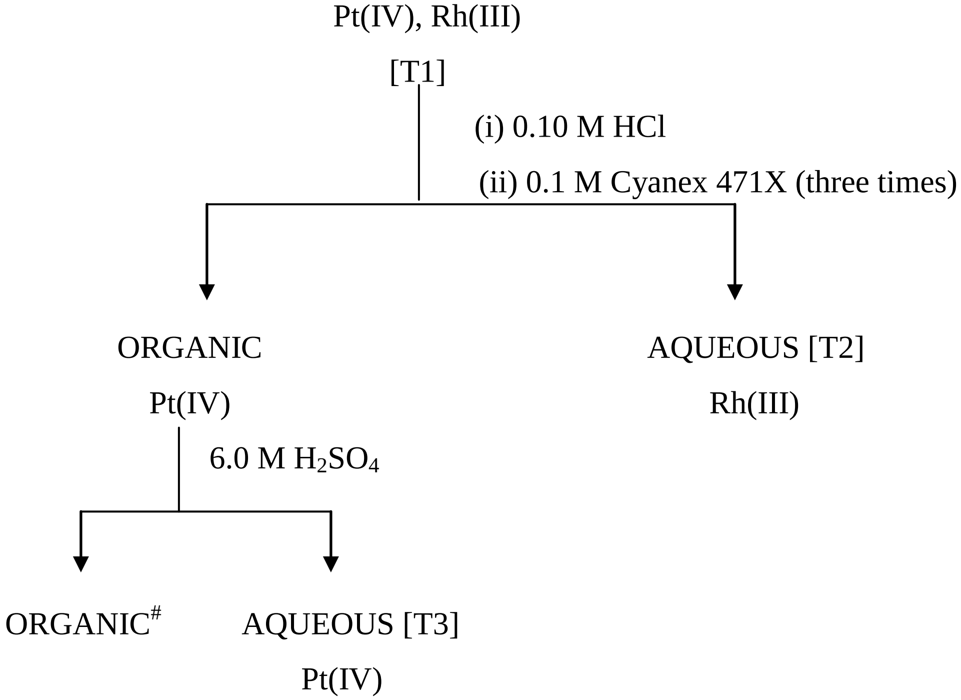
Note: '±' refers to the standard deviation
<0.05/<0.1 refers to the detection limit of the corresponding metal ion.

Table 4.6. Recovery of Pt(IV) and Rh(III) from thermocouple wire using 0.1 mol L^{-1} Cyanex 471X

Metal ions	Composition of initial solution [T1] (mg/l)	Composition of solution [T2] (mg/l)	Composition of solution [T3] (mg/l)	Recovery (%)	Purity (%)
Pt	6.80 ± 0.4	<0.05	6.76 ± 0.4	99.4	98.54
Rh	2.04 ± 0.2	2.11 ± 0.2	<0.1	100	97.68

Note: '±' refers to the standard deviation
<0.05/<0.1 refers to the detection limit of the corresponding metal ion.

Flowsheet 4.2: Recovery of Pt(IV) and Rh(III) from thermocouple wire using Cyanex 471X



organic phase can be regenerated by washing with water.

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CHAPTER V

EXTRACTION STUDIES ON Pt(IV), Ir(III), Rh(III) AND ASSOCIATED METAL IONS USING DEHPA

The separation of platinum group metals amongst themselves and from other elements coexisting in various ores and alloys has always posed a challenging exercise for the separation scientists. Furthermore, the potential environmental hazards of spent industrial and automotive catalysts call for putting an emphasis on the recycling of these waste materials. Recovery of expensive PGMs from spent commercial matrices opens up a new field for the extraction chemists. Various organophosphorus extractants have been explored to arrive at a plausible solution to some of the aforesaid problems. Higher cost of extractants makes high initial plant investments. Hence, there is a need to look for solvent extraction separation possibilities with low cost reagents such as DEHPA. DEHPA, di-(2-ethylhexyl) phosphoric acid (DEHPA) is a diester of phosphoric acid and 2-ethylhexanol. The choice of DEHPA as an extractant is due to its hydrophobic nature and therefore low aqueous solubility and a tendency to move out of water to other matrices. The extractant has by far received maximum attention due to its great potential for the extraction of a variety of metal ions (1-5).

DEHPA has been extensively used as an effective extractant for the extraction and separation of lanthanides and actinides. Reddy and group (6) investigated the extraction of Eu(III) and Tb(III) from thiocyanate medium using mixtures of 2-ethylhexylphosphonic acid mono-2-ethylhexyl ester (EHPNA) and DEHPA or TBP or TOPO or triphenylphosphine oxide (TPhPO) in benzene diluent. Thanh et al. (7) separated rare earths into three groups by six-stage counter current extraction with DEHPA. Green and Harbuck (8) investigated the recovery of yttrium from the ore of Bokan Mountain area origin. Yttrium was selectively extracted using a synergistic combination of octylphenyl acid phosphate (OPAP) and DEHPA. Yttrium was stripped directly as a solid using sodium hydroxide solution. Huang and associates (9) studied the removal of samarium from $NdCl_3$ solution using DEHPA as an extractant. Lee and coworkers (10) separated minor actinides and rare earths using DEHPA. Quantitative extraction of Am, Np and rare earths was achieved with DEHPA in dodecane. Am, rare earths and Np were selectively stripped employing mixture of DTPA and lactic acid, HNO_3 and $H_2C_2O_4$, respectively. Lim and his group (11) studied the kinetics of rare earth extraction into DEHPA using radiotracers in a modified Lewis cell. Yang et al. (12) carried out the separation of Am and Eu from nitrate medium containing zirconium with n-dodecane solution of DEHPA. Am and Eu were selectively stripped employing mixed solution of DTPA and lactic acid and HNO_3, respectively. Khofan and group (13) investigated the stripping of uranium from kerosene solution of DEHPA. Various reagents such as ammonium carbonate, phosphoric acid, sulphuric acid, hydrochloric acid and nitric acid were tested as strippants of uranium from kerosene solution of DEHPA. Stripping was measured at different operating conditions namely aqueous and organic phase concentrations and temperature. Striping was found to decrease by increasing concentration of DEHPA and was further depressed by adding TOPO as a synergist. Long et al. (14) studied the extraction of Ce(IV) with DEHPA in sulphonated kerosene. Various aqueous and organic phase variables have been studied. The extraction mechanism was proposed by slope analysis method. The developed method was applied to bastnaesite leached with sulphuric acid. Thakur (15) separated dysporium and yttrium from a fraction of rare earths obtained from monazite. The extractants DEHPA and 2-ethylhexyl 2-ethylhexyl phosphonic acid (EHEHPA-PC 88A) were employed for developing the process. Zamani and Yaftian (16) reported improved separation of thorium, lanthanum and europium ions by cyclohexane solution of DEHPA using 2-nitrobenzo-18-crown-6 (NB18C6) as a selective masking agent. NB18C6 was efficient masking agent towards lanthanide ions. Ribereiro and group (17) extracted uranium from digested solution of colofanite with a mixture of DEHPA and TOPO in kerosene. Thorium in the raffinate was extracted with TOPO in cyclohexane. Uranium was selectively stripped over iron using ammonium or sodium carbonate.

A voluminous literature is available on the use of DEHPA as an extractant for transition metals. Among the transitions metals DEHPA has been widely explored for the distribution studies involving zinc and cadmium. Cho and Dai (18) evaluated the separation of zinc, nickel, cobalt and manganese by selective extraction in a sequential operation with kerosene solutions of DEHPA, Cyanex 272 and LIX 84. The separation of iron from zinc with kerosene solution of DEHPA was investigated by Weert and his research group (19). They achieved the stripping of iron from loaded organic phase with nitric acid. Nogueira and Delmas (20) carried out the extraction studies on cadmium, cobalt and nickel using DEHPA and Cyanex 272. DEHPA was used for the selective extraction of cadmium and Cyanex 272 for cobalt. The designed flowsheet was applied to the Ni-Cd-Co containing residues and spent rechargeable batteries. Godinez and coworkers (21) investigated the separation of iron from zinc using DEHPA. The effects of various processing parameters have also been evaluated. Alamdari et al. (22) investigated the simultaneous extraction of zinc and cadmium by a mixture of DEHPA and mono-2-ethylhexyl phosphoric acid (MEHPA) in the presence of TBP as a modifier. The effects of temperature, pH and TBP concentration on the extraction of zinc and cadmium were determined. The extraction reaction was endothermic for zinc while exothermic for cadmium. Bartkowska and associates (23) studied the extraction of Zn(II), Fe(III) and Fe(II) with TBP and its binary mixture with DEHPA and Cyanex 302 from chloride medium. They accomplished the stripping of Zn(II) and Fe(III) in three successive stages using acidified water and 0.1 M H_2SO_4, respectively.

Sze and Xue (24) demonstrated the extraction of zinc and chromium with solvents containing DEHPA, PC-88A, Cyanex 272 and Cyanex 302 and recovered the said metals from alloy electroplating wastewater. Extraction of chromium required a higher pH than zinc. Among the four extractants, DEHPA performed the best. A flowsheet based on zinc extraction with DEHPA and chromium extraction with ammoniated DEHPA was developed. Alamdari and group (25) carried out simultaneous extraction of zinc and cadmium using a mixture of DEHPA and MEHPA. The effects of DEHPA and MEHPA concentration on co-extraction of zinc and cadmium have been determined. Studies on the selective separation of zinc and cadmium showed that the degree of separation decreased with the increasing MEHPA. Dakhil and Pincovschi (26) reported the extraction of zinc, copper and cadmium using DEPHA, TOPO and Cyanex 272 as extractants. Moraia and Benedetto (27) recovered zinc from industrial effluents using DEHPA. The recovery of zinc was more than 99%. Guerrs and researchers (28) separated zinc from manganese employing DEHPA as an extractant. The process was used for recycling spent Zn-MnO_2 batteries. Kasikova and others (29) extracted V(IV) employing the mixture of organophosphorus acids (DEHPA and Cyanex 272). A comparison of the extraction behaviour of vanadium in +4 and +5 oxidation states was also performed. The developed process was applied to the aqueous leach of used vanadium catalysts. Avila et al. (30) assessed the feasibility of DEHPA, Cyanex 272 and Ionquest 290 for the recovery of zinc from an acidic mine effluent. The equilibrium was reached in less than five minutes with the said extractants. Among the three extractants studied, Ionquest 290 was found to be the most suitable. Agarwal et al. (31) studied the separation of cadmium, from cobalt and nickel, using DEHPA. The conditions were optimized for the selective recovery of Cd using 20% DEHPA with 60% saponification. The dependence of extraction on pH indicated that the extraction of Cd(II) proceeded according to a cation-exchange reaction at lower acidity and solvating reaction at higher acidities. The co-extracted Ni and Co were effectively scrubbed with $CdSO_4$ at pH 0.5. Cd was quantitatively stripped from the loaded DEHPA with H_2SO_4. Based on the slope analysis, cadmium was found to be extracted as $CdR_2.(HR)_2$.

Juan and group (32) studied the extraction of Cr(III) with kerosene solution of DEHPA containing isodecanol. Solutions of sodium hydroxide and hydrogen peroxide were used for stripping. Moris et al. (33) explored Alamine 336 and DEHPA for the extraction of tungsten and molybdenum. They found that Alamine 336 extracts both tungsten and molybdenum whereas DEHPA selectively extracts molybdenum in the presence of tungsten. Juang and Ju (34) studied the extraction of Cu(II) using kerosene solution of DEHPA from sulphate medium in the presence of complexing agents namely EDTA, nitrilotriacetic acid (NTA) and citric acid. The extraction efficiency of Cu(II) decreased with the addition of EDTA and NTA, but not with citric acid. The co-extraction of citric acid into the organic phase could explain the increase in extraction efficiency with increasing citric acid concentration. The presence of complexing agents resulted in a change of reaction stoichiometry of Cu(II) and DEHPA due to the mutual interaction of Cu(II)-DEHPA complexes and the complexing agents.

Rane et al. (35) recovered cobalt from spent ammonia cracking catalyst after leaching with sulphuric acid. They removed Fe(III) and Al(III) from the leach liquor either by chemical precipitation or solvent extraction using DEHPA. When nickel was present as an impurity, it was separated by extraction with LIX 84I. Yaruro et al. (36) evaluated the extraction process to separate barium with kerosene solution of DEHPA and iso-propanol as a modifier. Different phase variables were studied. A recovery of ~90% was obtained using 30% DEHPA and the modifier. Kul and Cetinkaya (37) investigated the extraction and recovery of nickel using kerosene solution of DEHPA and LIX 984N-C. LIX was not recommended for the said purpose due to emulsion formation. The developed scheme was applied for the recovery of zinc from nickel electroplating second rinse bath solution. Sousa and coworkers (38) studied the modeling of cobalt and nickel extraction by solvent extraction in sulphate medium with DEHPA in isoparaffin. The values of distribution coefficients predicted by the model of Co(II) and Ni(II) extraction were in good agreement with experimental values. Kinetics of the extraction of various metals employing DEHPA by the single drop technique has also been reported (39-44).

From the above discussion it is evident that a sizeable literature is available on DEHPA and most of the reported work is on d-block and f-block elements. Inspite of the inherent utility of DEHPA, no systematic extraction studies were undertaken on PGMs. Thus it was thought interesting to investigate the extraction behaviour of PGMs using DEHPA. As a first step, the conditions for the distribution of Pt(IV), Ir(III), Rh(III), Ru(III) and Pd(II) were identified by studying their extraction behaviour from hydrochloric, sulphuric and nitric acid media. Detailed studies were carried out on Pt(IV) and Ir(III). The effect of phase variables such as equilibration time, nature of diluent and concentration of acid and extractant on the extraction was investigated. The stripping of extracted metal ions was tested with various strippants. The stability of DEHPA towards long term contact with acid has been ascertained and the regeneration capacity checked. The loading capacity of the extractant was also assessed. The extraction behaviour of some associated metal ions namely Au(III), Fe(III), Cr(III), Cu(II), Ni(II), Co(II), Fe(II) and Ag(I)in DEHPA was also observed. The distribution data of various metal ions have been utilized to obtain some important binary separations involving Pt(IV)/Ir(III)/Rh(III). Stimulated by these results a scheme has been developed for the recovery of Pt(IV), Ir(III) and Rh(III).

Results and Discussion

Extraction behaviour of Pt(IV), Ir(III), Rh(III), Ru(III) and Pd(II) from $HCl/H_2SO_4/HNO_3$ using 0.10 mol L^{-1} toluene solution of DEHPA

The trend of extraction of Pt(IV), Ir(III), Rh(III), Ru(III) and Pd(II) in toluene solution of DEHPA (0.10 mol L^{-1}) from $HCl/H_2SO_4/HNO_3$ (0.10 – 6.0 mol L^{-1}) is shown in figures 5.1, 5.2 and 5.3. The percent extraction of Pt(IV) from chloride medium ranges between 60 and 70% in the investigated range of acid molarity. In the case of sulphate medium Pt(IV) shows maximum extraction (~30%) at 0.50 mol L^{-1} acidity and then decreases to become negligible at 6.0 mol L^{-1} H_2SO_4. The extraction of Pt(IV) from HNO_3 medium is negligible in the entire investigated range of acid molarity. The extraction of Ir(III) is around 45% at 0.10 mol L^{-1} HCl which increases with the increase in acidity and attains a maximum value (~60%) at 6.0 mol L^{-1} HCl. The extraction of Ir(III) from sulphuric acid medium is almost constant (40-50%) in the studied acidity range. Ir(III) shows quantitative extraction between 0.5 and 1.0 mol L^{-1} HNO_3 which decreases on increasing or decreasing the acid molarity. The extraction of Ru(III) remains more or less constant (23-35%) in all the three mineral acids in the investigated range of acid molarity. Rh(III) and Pd(II) show low or negligible extraction in all the three mineral acids.

Preliminary studies carried out on the extraction behavior of various PGMs with DEHPA indicated low extraction of Rh(III) and poor extraction of Ru(III) and Pd(II) from

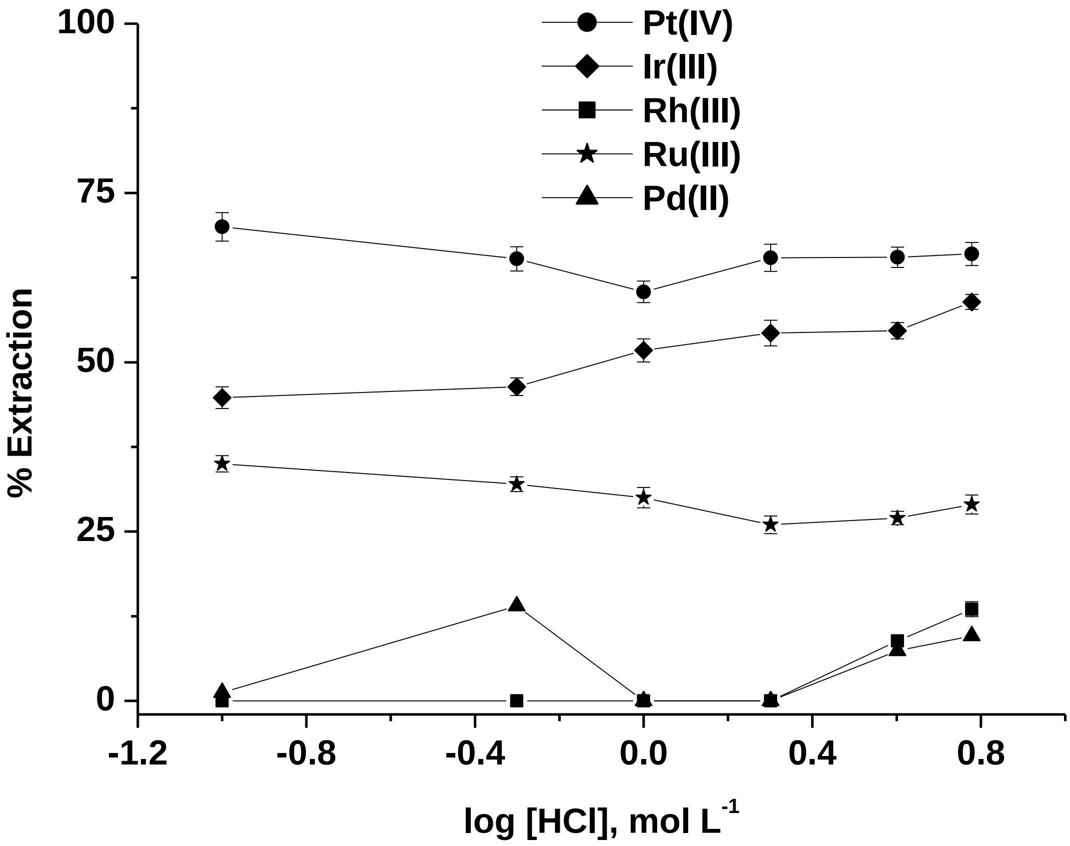


FIGURE 5.1: Effect of concentration of hydrochloric acid on the extraction of Pt(IV), Ir(III), Rh(III), Ru(III) and Pd(II)

Conditions

[DEHPA = 0.10 mol L^{-1}

[Metal ion] = 5 x 10^{-4} mol L^{-1}

[HCl] = 0.1 - 6.0 mol L^{-1}

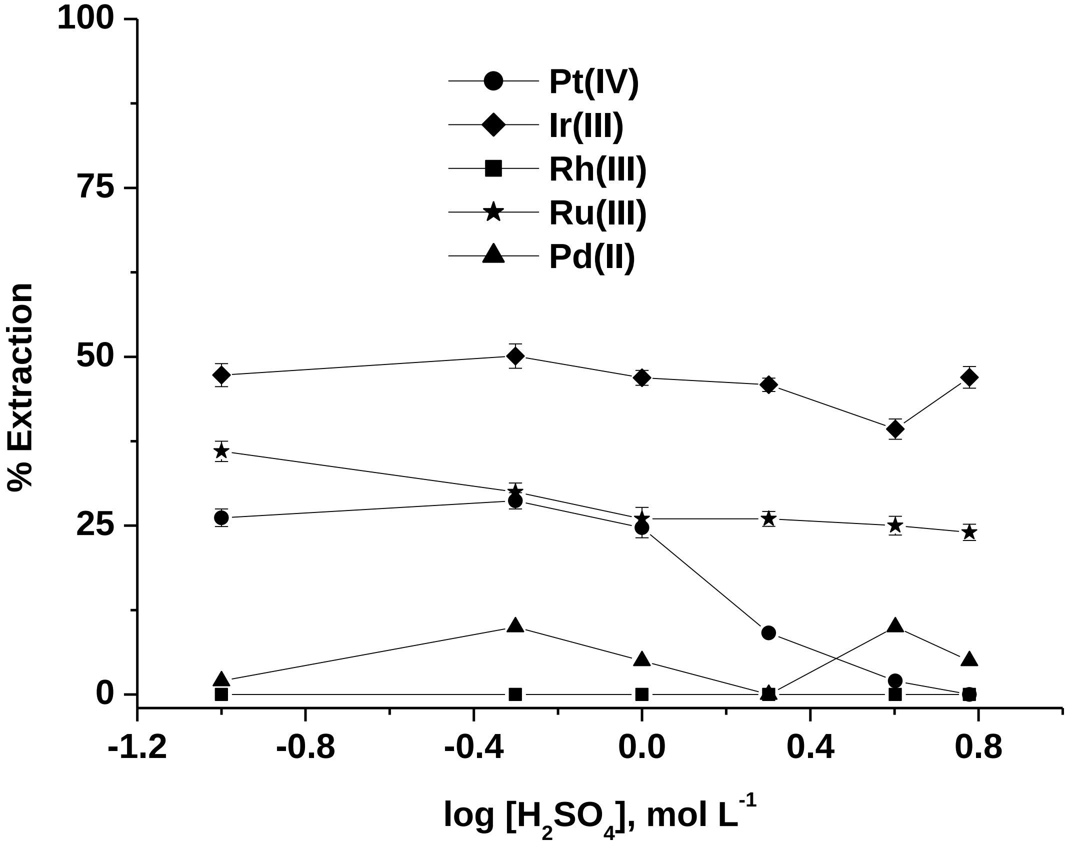


FIGURE 5.2: Effect of concentration of sulphuric acid on the extraction of Pt(IV), Ir(III), Rh(III), Ru(III) and Pd(II)

Conditions

[DEHPA] = 0.10 mol L^{-1}

[Metal ion] = 5 x 10^{-4} mol L^{-1}

[H_2SO_4] = 0.1 - 6.0 mol L^{-1}

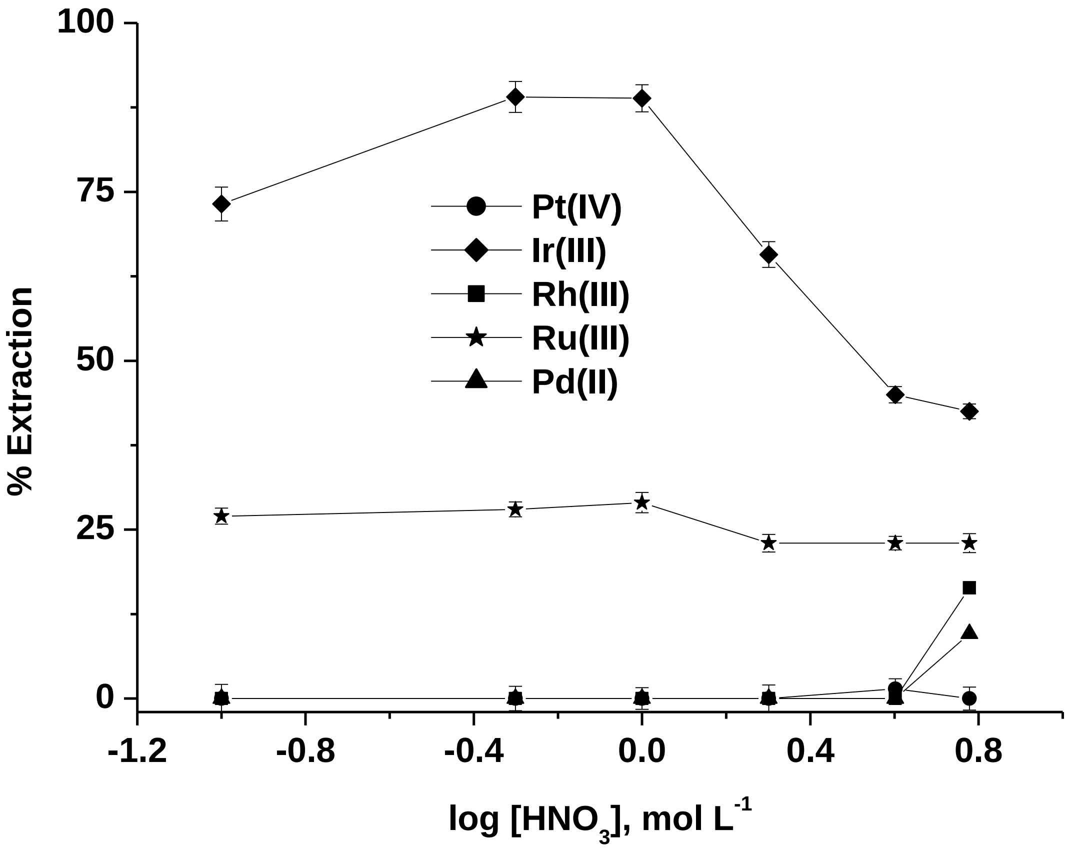


FIGURE 5.3: Effect of concentration of nitric acid on the extraction of Pt(IV), Ir(III), Rh(III), Ru(III) and Pd(II)

Conditions

[DEHPA] = 0.10 mol L^{-1}

[Metal ion] = 5 x 10^{-4} mol L^{-1}

[HNO_3] = 0.1 - 6.0 mol L^{-1}

all the three mineral acid media. Therefore detailed distribution studies were carried out on Pt(IV) and Ir(III) using DEHPA as an extractant. Detailed distribution studies were conducted at 1.0 mol L^{-1} HCl (Pt(IV)) and 2.0 mol L^{-1} HNO_3 (Ir(III)) using 0.1 mol L^{-1} DEHPA.

Effect of equilibration time

The variation in percent extraction of Pt(IV) and Ir(III) as a function of varying shaking time (1 – 30 min) is shown in figure 5.4. It is apparent that a minimum of four minutes contact time is sufficient for attaining limiting extraction for both the metal ions. Therefore in all further studies the two phases were contacted for six minutes. It was observed that prolonged shaking does not affect the results.

Effect of temperature on the extraction

The effect of temperature (10^o-50^oC) on the distribution of Pt(IV) and Ir(III) was investigated at 1.0 mol L^{-1} HCl and 2.0 mol L^{-1} HNO_3 using 0.10 mol L^{-1} toluene solution of DEHPA. An increase in extraction with the increase in temperature was observed indicating both the processes to be endothermic. Plots between 1000/T and log K_{ex} (figure 5.5) gave straight lines with a negative slope values of 0.27 and 0.79, for Pt(IV) and Ir(III), respectively. The values of ΔH as calculated using Van't Hoff equation $-\ln K_{ex} = \Delta H/R.1/T$, were found to be -5.12 kJ/mol and -0.80 kJ/mol, for Pt(IV) and Ir(III), respectively.

Effect of extractant concentration

The effect of varying extractant concentration (0.001-0.50 mol L^{-1}) on the distribution of Pt(IV) and Ir(III) is illustrated in figure 5.6. The extraction of both the metal ions increases with the increasing extractant concentration. The log-log plots between the extractant concentration and distribution ratio gave slope values of around one. The results thus indicate the stoichiometry of the extracting species to be 1:1 (metal:extractant).

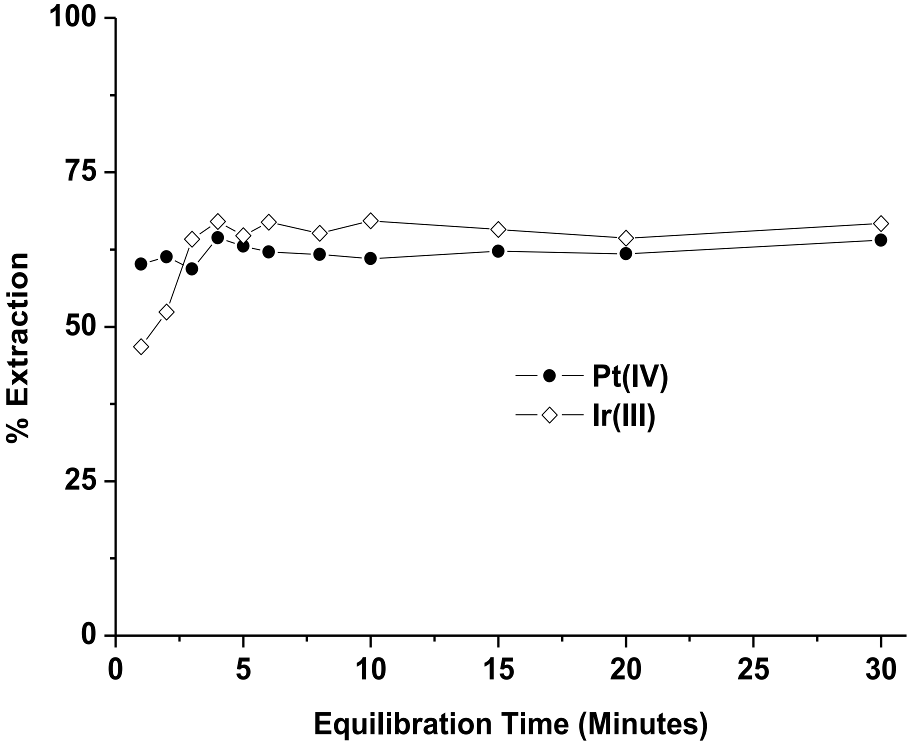


FIGURE 5.4: Effect of equilibration time on the extraction of Pt(IV) and Ir(III)

Conditions

[DEHPA] = 0.10 mol L^{-1}

[Metal ion] = 5 x 10^{-4} mol L^{-1}

[HCl] = 1.0 mol L^{-1} (Pt(IV))

[HNO_3] = 2.0 mol L^{-1} (Ir(III))

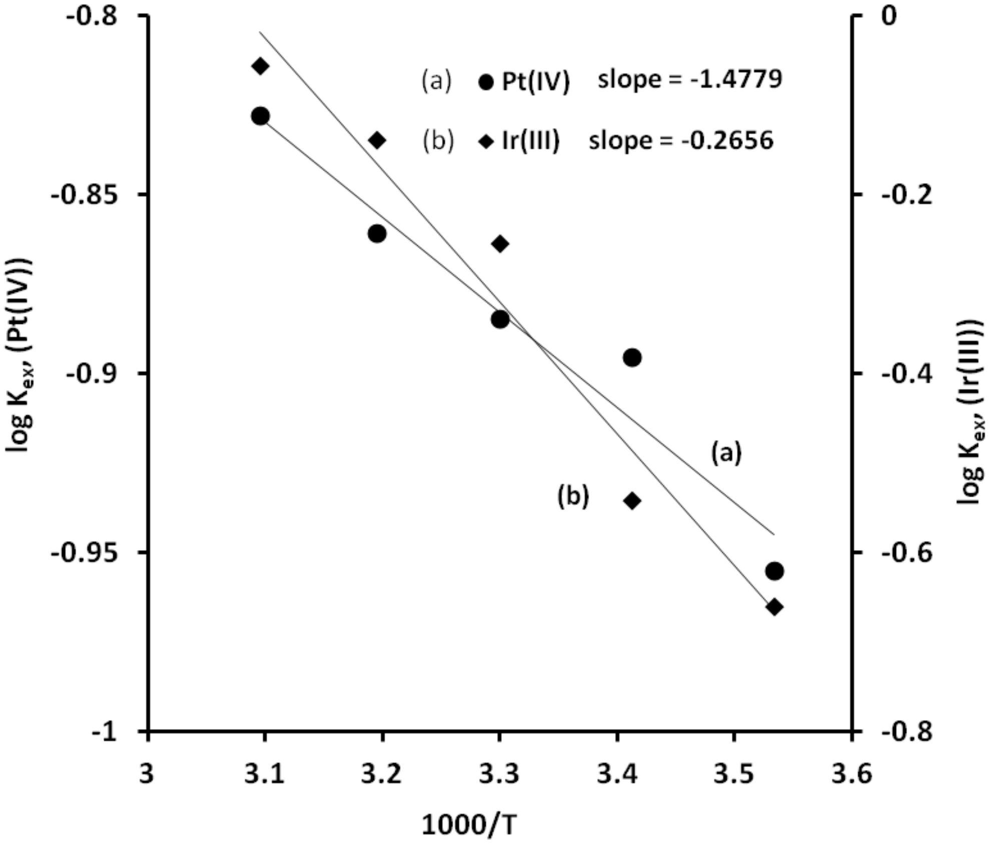


FIGURE 5.5: Effect of temperature on the extraction of Pt(IV) and Ir(III)

Conditions

[DEHPA] = 0.10 mol L^{-1}

[Metal ion] = 5 x 10^{-4} mol L^{-1}

[HCl] = 1.0 mol L^{-1} (Pt(IV))

[HNO_3] = 2.0 mol L^{-1} (Ir(III))

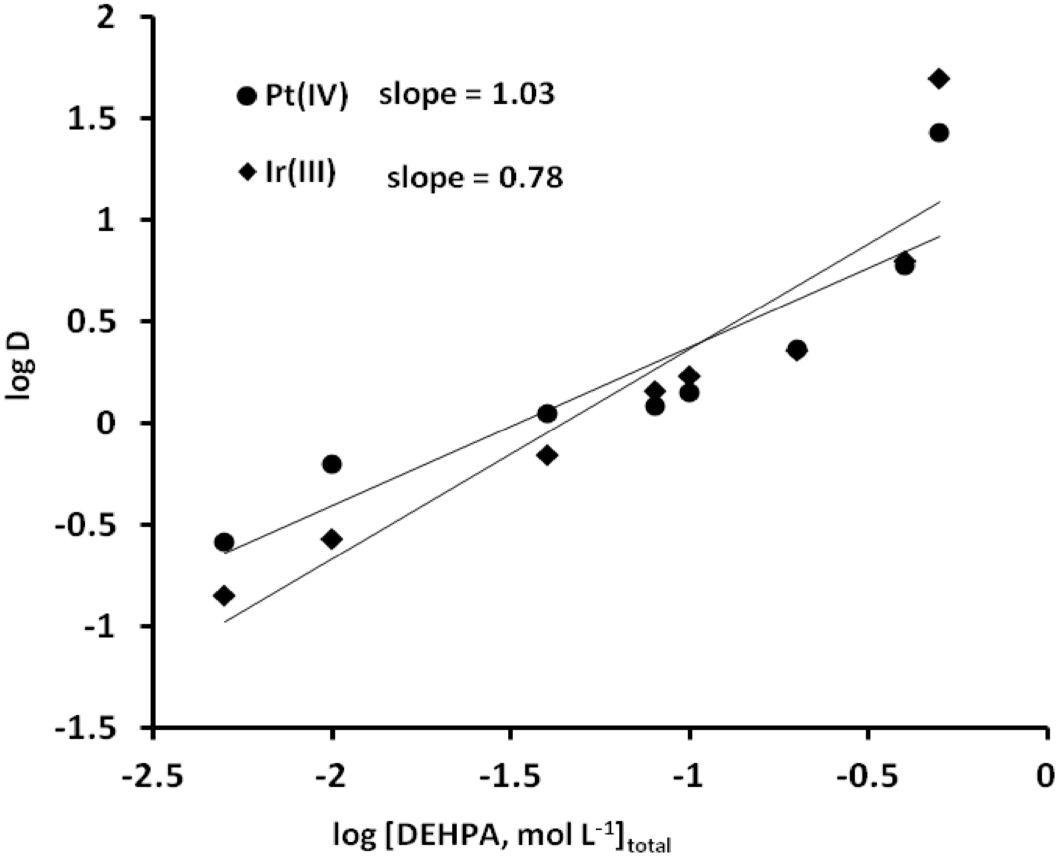


FIGURE 5.6: Effect of extractant concentration on the extraction of Pt(IV) and Ir(III)

Conditions

[DEHPA] = 0.10 mol L^{-1}

[Metal ion] = 5 x 10^{-4} mol L^{-1}

[HCl] = 1.0 mol L^{-1} (Pt(IV))

[HNO$_3$] = 2.0 mol L^{-1} (Ir(III))

Effect of the nature of diluent

The solvents of varying nature were employed as diluents for the extraction of Pt(IV) and Ir(III) in 0.10 mol L^{-1} DEHPA. The distribution data for both the metal ions using nitrobenzene, cyclohexane, chloroform, toluene, xylene, kerosene and n-hexane is given in table 5.1. It is apparent from the table that in both the cases no regular trend is discrenable as the extractions are almost similar in all the solvents. Toluene has been used as diluent for all the other studies since it provides quicker phase separation.

Loading Capacity of DEHPA towards Pt(IV) and Ir(III)

The loading capacity of DEHPA (0.10 mol L^{-1}) for Pt(IV) was evaluated by equilibrating Pt(IV) solution at 0.10 mol L^{-1} HCl at a fixed organic to aqueous phase ratio of 1:1. The two phases were separated and the metal ion concentration transferred to the organic phase was determined. The same organic phase was used again for the extraction of Pt(IV) from a fresh aqueous phase (figure 5.7). This procedure was repeated till no further extraction of Pt(IV) in the organic phase was observed. The maximum loading obtained is 54 mM Pt(IV) per 0.10 M extractant after thirteenth stage.

The loading capacity of DEHPA for Ir(III) was determined at 0.50 mol L^{-1} HNO_3 using the same procedure. The maximum loading observed was 43 mM Ir(III) per 0.10 M extractant after twelfth stage of contact.

Stability and regeneration capacity of the extractant

The stability of DEHPA was assessed by keeping 0.10 mol L^{-1} extractant solution in contact with 6.0 mol L^{-1} HCl (for Pt(IV)) and 6.0 mol L^{-1} HNO_3 (for Ir(III)) with intermittent shaking. A known aliquot of the extractant was removed periodically after five days, washed with water and then used for the extraction of Pt(IV)/Ir(III) at an appropriate acid molarity. The variation in the extraction of Pt(IV) and Ir(III) is shown in figure 5.8. The results indicate an insignificant change in the percent extraction of Pt(IV) and Ir(III) even after an acid contact of forty days. A sharp decrease in percent extraction was observed after forty days of contact.

Table 5.1. Effect of the nature of various diluents on the extraction of Pt(IV) and Ir(III).

Diluent	Dielectric constant	Percent extraction	
		Pt(IV)	Ir(III)
Nitrobenzene	35.70	61.68	65.91
Cyclohexane	18.3	61.37	64.74
Chloroform	4.81	63.32	63.72
Toluene	2.44	62.12	65.12
Xylene	2.20	61.77	65.36
Kerosene	2.02	63.48	65.19
n-hexane	1.891	58.28	62.28

Conditions

[DEHPA] = 0.10 mol L^{-1}

[Metal ion] = 5 x 10^{-4} mol L^{-1}

[HCl] = 1.0 mol L^{-1} (Pt(IV))

[HNO_3] = 2.0 mol L^{-1} (Ir(III))

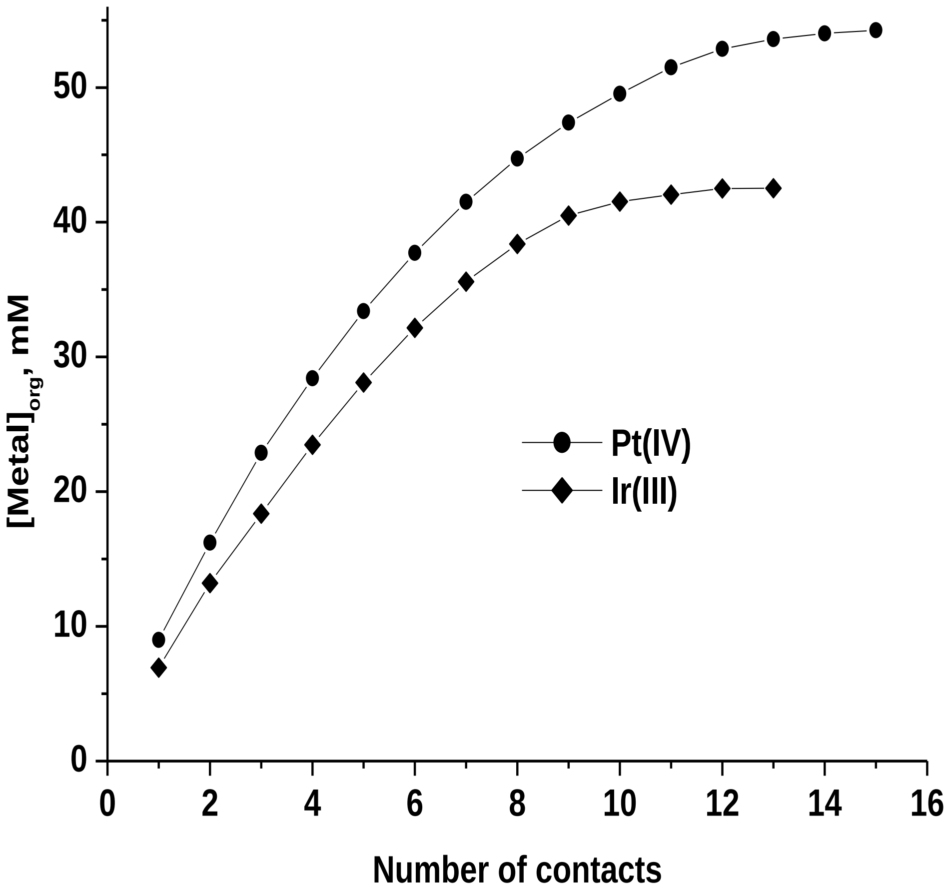


FIGURE 5.7: Loading capacity of DEHPA towards Pt(IV) and Ir(III)

Conditions

[Cyanex 471X] = 0.10 mol L^{-1}

[Metal ion] = 5 x 10^{-4} mol L^{-1}

[HCl] = 1.0 mol L^{-1} (Pt(IV))

[HNO_3] = 2.0 mol L^{-1} (Ir(III))

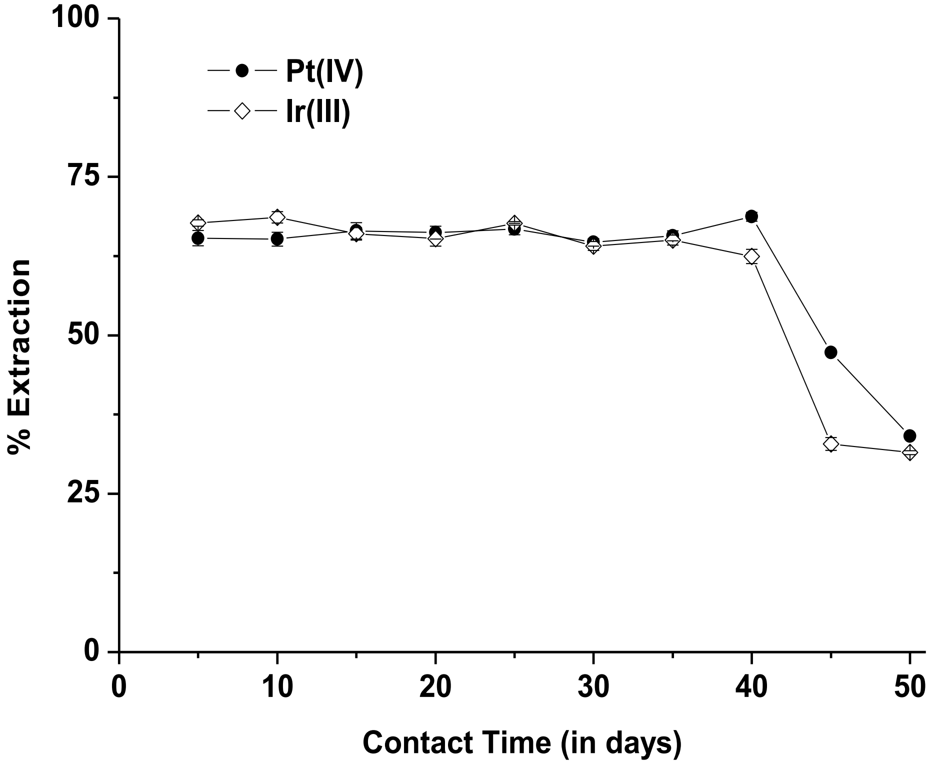


FIGURE 5.8: Variation in the extraction of Pt(IV)/Ir(III) using DEHPA solution kept in contact with 6.0 mol L^{-1} HCl/HNO_3

Conditions

[DEHPA] = 0.10 mol L^{-1}

[Metal ion] = 5 x 10^{-4} mol L^{-1}

[HCl] = 6.0 mol L^{-1} (Pt(IV))

[HNO_3] = 6.0 mol L^{-1} (Ir(III))

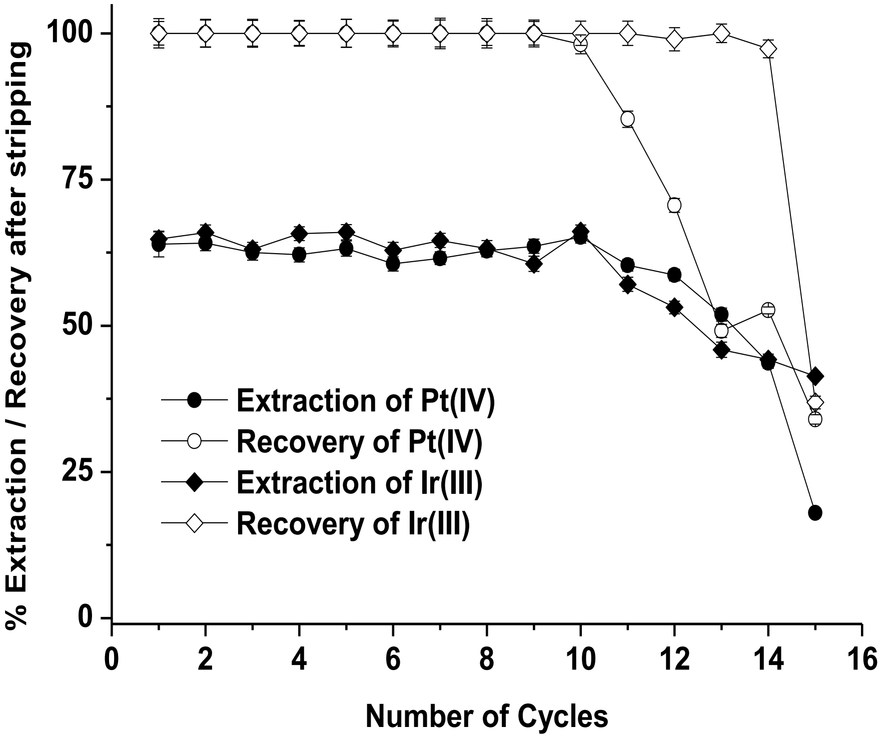


FIGURE 5.9: Variation in the extraction / recovery of Pt(IV)/Ir(III) in successive

Conditions

[DEHPA] = 0.10 mol L^{-1}

[Metal ion] = 5 x 10^{-4} mol L^{-1}

[HCl] = 1.0 mol L^{-1} (Pt(IV))

[HNO_3] = 2.0 mol L^{-1} (Ir(III))

[Strippant] = 5.0 mol L^{-1} $HClO_4$ (for Pt(IV))

= acidic 0.10 mol L^{-1} thiourea (for Ir(III))

The regeneration capacity of DEHPA was determined by carrying out successive extraction and stripping cycles for Pt(IV) and Ir(III). In between two cycles the organic phase was washed with water until the washings were almost neutral. The recovery of each step was calculated from the amount of metal ion that was extracted in the organic phase in that particular cycle. The variation in the extraction / stripping of metal ions is shown in figure 5.9. There is practically an insignificant change in the percent extraction / stripping of Pt(IV) and Ir(III) up to ten cycles.

Stripping reagents

Several aqueous solutions were employed for the stripping of Pt(IV) and Ir(III). The composition of strippants and their efficiency to strip Pt(IV) and Ir(III) are given in table 5.2. Data predicted that 5.0 mol L^{-1} $HClO_4$ was suitable for the quantitative stripping of Pt(IV) and 5.0 mol L^{-1} $HClO_4$ and 0.1 mol L^{-1} thiourea solution in 1.0 mol L^{-1} $HClO_4$ for Ir(III).

Extraction behaviour of associated metal ions

The extraction behaviour of associated metal ions was investigated only from HCl and HNO_3 media as Pt(IV) and Ir(III) exhibited maximum extraction from HCl and HNO_3, respectively.

HCl

The extraction behaviour of associated metal ions, namely Au(III), Cr(III), Fe(III), Cu(II), Ni(II), Co(II) and Fe(II) from HCl medium (0.10 to 6.0 mol L^{-1}) is shown in figure 5.10. The data indicate negligible extraction of all the studied associated metal ions except Fe(III) in the entire range of investigation. Maximum extraction (~70%) of Fe(III) is achieved at 0.1 mol L^{-1} acid which gradually decreases with the increasing acid molarity.

HNO_3

The extraction behaviour of different associated metal ions, namely Au(III), Cr(III), Fe(III), Cu(II), Ni(II), Co(II), Fe(II) and Ag(I) from nitric acid medium (0.10 to 6.0

Table 5.2. Efficiency of various stripping reagents for Pt(IV) and Ir(III).

Strippant used	% Stripping	
	Pt(IV)	Ir(III)
5.0 mol L^{-1} $HClO_4$	91.53	100
0.10 mol L^{-1} EDTA	10.45	17.79
6.0 mol L^{-1} H_2SO_4	7.04	64.50
0.10 mol L^{-1} Thiourea	11.68	33.83
0.10 mol L^{-1} Thiourea + 1.0 mol L^{-1} HNO_3	51.47	49.36
0.10 mol L^{-1} Thiourea + 1.0 mol L^{-1} $HClO_4$	35.72	100
0.10 mol L^{-1} Thiourea + 1.0 mol L^{-1} HCl	58.23	71.00

Conditions:

[DEHPA] = 0.1 mol L^{-1}
[Metal ion] = 5 x 10^{-4} mol L^{-1}
[HCl] = 1.0 mol L^{-1} for Pt(IV)
[HNO_3] = 2.0 mol L^{-1} for Ir(III)
Organic:aqueous = 1:1

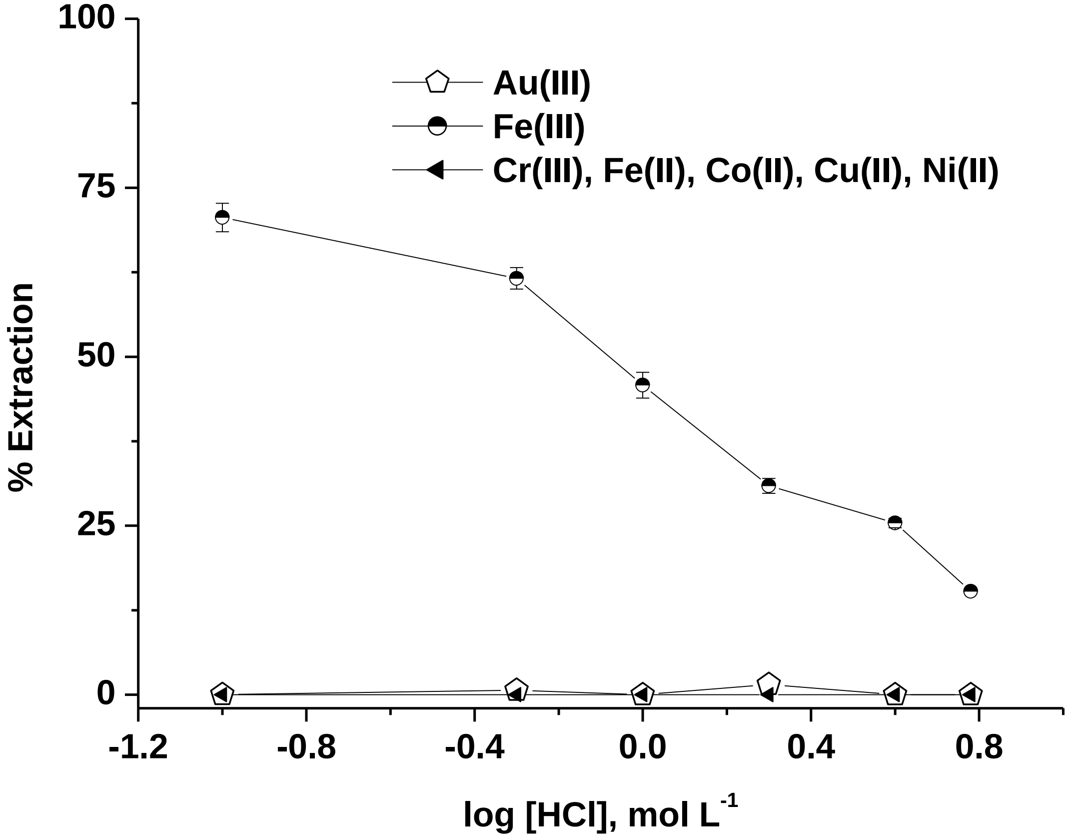


FIGURE 5.10: Effect of concentration of hydrochloric acid on the extraction of associated metal ions

Conditions

[DEHPA] = 0.10 mol L^{-1}

[Metal ion] = 5 x 10^{-4} mol L^{-1}

[HCl] = 0.1 - 6.0 mol L^{-1}

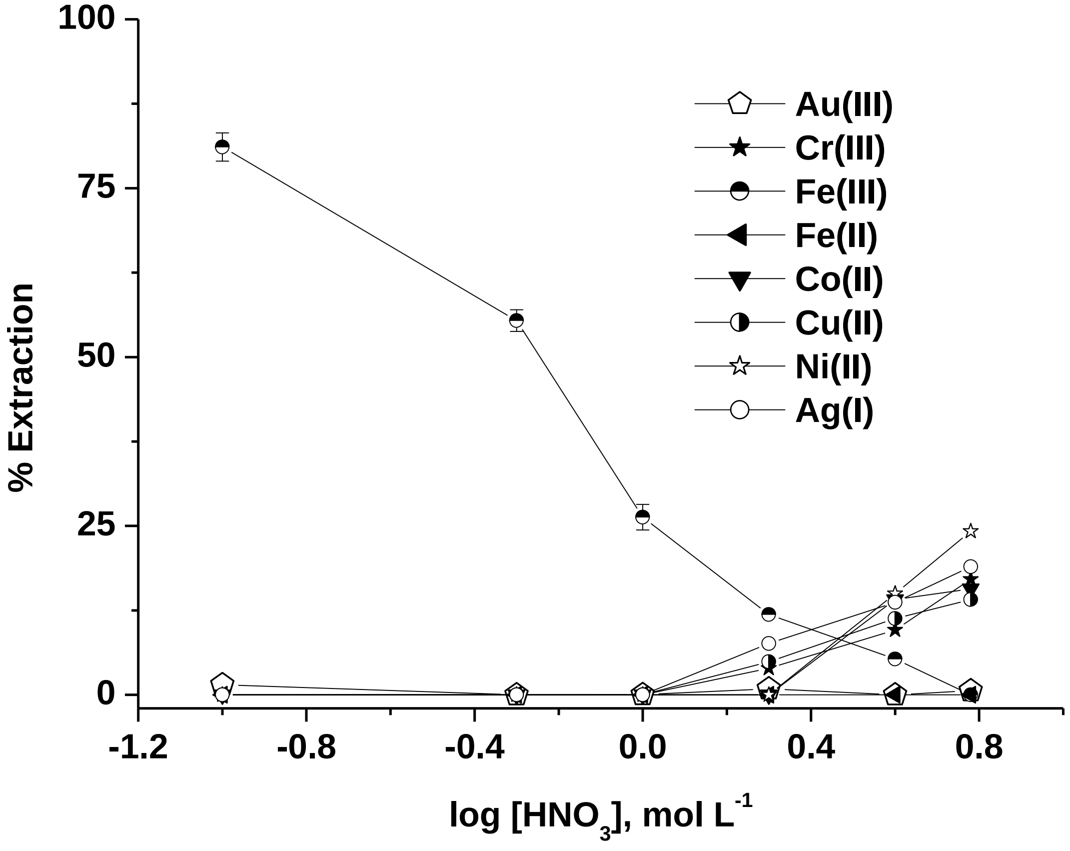


FIGURE 5.11: Effect of concentration of sulphuric acid on the extraction of associated metal ions

Conditions

[DEHPA] = 0.10 mol L^{-1}

[Metal ion] = 5 x 10^{-4} mol L^{-1}

[HNO_3] = 0.1 - 6.0 mol L^{-1}

mol L^{-1}) is shown in figure 5.11. As depicted in figure the extraction of Au(III) and Fe(II) is negligible in the entire range of investigation. The extraction trends of Cr(III), Cu(II), Ni(II), Co(II) and Ag(I) are almost similar with negligible extraction at low acidity followed by a gradual increase with the increase in acidity. Fe(III) shows maximum extraction (~80%) at 0.1 mol L^{-1} HNO_3 which sharply decreases to negligible extraction at 6.0 mol L^{-1} HNO_3.

Separations

The potential of DEHPA for attaining some important binary separations of Pt(IV) and Ir(III) has been explored. The conditions of separations along with the percent recovery of metal ions are mentioned in tables 5.3 and 5.4.

Binary separations

Pt(IV)

The extraction behaviour of Pt(IV) from HCl medium is quite different from most of the associated metal ions, therefore the separation of Pt(IV) from other associated metal ions was carried out from HCl medium. Pt(IV) is selectively extracted from an aqueous solution containing Rh(III)/Au(III)/Cr(III)/Cu(II)/Ni(II)/Co(II)/Fe(II) at 0.10 mol L^{-1} HCl using 0.1 mol L^{-1} DEHPA. In order to achieve Pt(IV)-Fe(III) separation, Fe(III) was first reduced to Fe(II) using ascorbic acid followed by the extraction of Pt(IV) at 0.10 mol L^{-1} HCl leaving Fe(II) in the aqueous phase. In each case the aqueous and organic phases were equilibrated thrice for quantitative transfer of Pt(IV) from aqueous to organic phase. In all the above cases Pt(IV) was recovered by equilibrating the loaded organic phase thrice with 5.0 mol L^{-1} $HClO_4$.

Ir(III)

The separation of Ir(III) from the associated metal ions has been achieved at 0.50 mol L^{-1} HNO_3. At this acidity around 90% Ir(III) is extracted leaving Pt(IV)/Rh(III)/Au(III)/ Cr(III)/Cu(II)/Ni(II)/Co(II)/Fe(II)/Ag(I) in the aqueous phase. To separate Fe(III) from Pt(IV) it was reduced to Fe(II) with ascorbic acid prior to separation. Moreover, the aqueous and organic phases were equilibrated twice to achieve quantitative transfer of Ir(III) into the organic phase. Ir(III) was stripped from the organic phase using 0.10 mol L^{-1} thiourea solution in 1.0 mol L^{-1} $HClO_4$.

Recovery of Pt(IV), Ir(III) and Rh(III) from synthetic mixture using DEHPA

The conditions of proposed binary separations were fused together to design a flowsheet for the separation and recovery of Pt(IV), Ir(III) and Rh(III) from synthetic solution using DEHPA. 50 mL of an aqueous solution [A1] containing equimolar concentrations of Pt(IV), Ir(III) and Rh(III) at 0.10 mol L^{-1} HNO_3 were equilibrated twice with equal volume of 0.10 mol L^{-1} toluene solution of DEHPA. This step resulted in quantitative transfer of Ir(III) into the organic phase while Pt(IV) and Rh(III) remained in the raffinate [A2] which was evaporated to near dryness. The residue was dissolved in HCl adjusting the final acidity to 0.10 mol L^{-1} HCl and final volume to 50 mL. The resulting solution was then equilibrated thrice with equal volume of 0.10 mol L^{-1} DEHPA which extracted the Pt(IV) leaving Rh(III) in the aqueous phase [A3]. The extracted Pt(IV) was then recovered by equilibrating the loaded organic phase thrice with 5.0 mol L^{-1} $HClO_4$ [A4]. The organic phase containing Ir(III) was treated with acidic 0.10 mol L^{-1} thiourea [A5] in order to recover Ir(III). The concentration of the metal ions in the initial and the recovered solutions are given in table 5.5. The flowsheet 5.1 can be employed to recover platinum, iridium and rhodium from real samples.

Table 5.3. Binary separations of Pt(IV) using 0.10 mol L^{-1} DEHPA

Metal ions separated*	Molar ratio	Acid molarity (mol L^{-1}), HCl	Metal ion remaining in the aqueous phase (%)	Metal ion transferred into the organic phase (%)	Recovery of metal ion from the organic phase (%)[a]	Separation factor, β (based on single extraction)
Pt(IV):Rh(III)	1:10	0.1	99 ± 1.0, Rh	99 ± 1.0, Pt	98 ± 1.1, Pt	8.7×10^3
	10:1		100 ± 1.0, Rh	99 ± 1.1, Pt	99 ± 0.8, Pt	8.0×10^3
Pt(IV):Au(III)	1:10	0.1	99 ± 1.0, Au	99 ± 1.1, Pt	99 ± 1.1, Pt	8.2×10^3
	10:1		100 ± 1.0, Au	99 ± 1.2, Pt	98 ± 1.2, Pt	1.0×10^4
Pt(IV):Cr(III)	1:10	0.1	99 ± 1.0, Cr	98 ± 1.1, Pt	98 ± 1.0, Pt	1.2×10^4
	10:1		99 ± 1.1, Cr	99 ± 1.3, Pt	99 ± 1.1, Pt	1.4×10^4
Pt(IV):Cu(II)	1:10	0.1	99 ± 1.1, Cu	99 ± 0.9, Pt	100 ± 1.1, Pt	8.9×10^3
	10:1		100 ± 0.5, Cu	99 ± 1.0, Pt	100 ± 1.0, Pt	5.0×10^4
Pt(IV):Ni(II)	1:10	0.1	99 ± 1.1, Ni	97 ± 1.0, Pt	98 ± 1.0, Pt	1.3×10^4
	10:1		99 ± 1.0, Ni	98 ± 0.9, Pt	100 ± 0.9, Pt	1.0×10^4
Pt(IV):Co(II)	1:10	0.1	100 ± 0.6, Co	98 ± 1.0, Pt	97 ± 0.9, Pt	9.9×10^3
	10:1		99 ± 1.1, Co	98 ± 1.1, Pt	98 ± 1.0, Pt	9.2×10^3
Pt(IV):Fe(II)	1:10	0.1	100 ± 0.7, Fe	99 ± 1.0, Pt	98 ± 1.2, Pt	1.1×10^4
	10:1		100 ± 0.6, Fe	99 ± 0.9, Pt	99 ± 1.1, Pt	8.0×10^3

Note: '±' refers to the standard deviation

*The aqueous phase was equilibrated thrice with the equal volume of organic phase

[a] Pt(IV) was recovered by equilibrating thrice with 5.0 mol L^{-1} $HClO_4$

Table 5.4. Binary separations of Ir(III) using 0.10 mol L^{-1} DEHPA

Metal ions separated*	Molar ratio	Acid molarity (mol L^{-1}), HNO_3	Metal ion remaining in the aqueous phase (%)	Metal ion transferred into the organic phase (%)	Recovery of metal ion from the organic phase (%)[a]	Separation factor, β (based on single extraction)
Ir(III):Pt(IV)	1:10	0.5	99 ± 0.9, Pt	99 ± 0.9, Ir	100 ± 0.6, Ir	3.4×10^4
	10:1		100 ± 0.5, Pt	99 ± 1.1, Ir	99 ± 1.1, Ir	4.6×10^4
Ir(III):Rh(III)	1:10	0.5	99 ± 0.9, Rh	99 ± 0.8, Ir	98 ± 0.9, Ir	3.6×10^4
	10:1		99 ± 1.1, Rh	99 ± 1.2, Ir	99 ± 1.0, Ir	4.2×10^4
Ir(III):Au(III)	1:10	0.5	100 ± 1.1, Au	100 ± 0.8, Ir	99 ± 0.8, Ir	3.6×10^4
	10:1		99 ± 1.0, Au	99 ± 0.9, Ir	99 ± 0.9, Ir	3.0×10^4
Ir(III):Cr(III)	1:10	0.5	99 ± 0.8, Cr	98 ± 1.0, Ir	100 ± 0.5, Ir	5.1×10^4
	10:1		99 ± 0.9, Cr	98 ± 1.1, Ir	99 ± 1.0, Ir	3.3×10^4
Ir(III):Cu(II)	1:10	0.5	99 ± 1.0, Cu	99 ± 0.9, Ir	99 ± 1.1, Ir	4.7×10^4
	10:1		100 ± 0.5, Cu	99 ± 1.0, Ir	99 ± 1.0, Ir	3.9×10^4
Ir(III):Ni(II)	1:10	0.5	99 ± 0.9, Ni	98 ± 1.0, Ir	98 ± 0.9, Ir	4.0×10^4
	10:1		99 ± 1.1, Ni	99 ± 1.2, Ir	99 ± 1.0, Ir	4.3×10^4
Ir(III):Co(II)	1:10	0.5	99 ± 1.0, Co	99 ± 0.8, Ir	99 ± 1.0, Ir	4.0×10^4
	10:1		99 ± 1.0, Co	98 ± 1.0, Ir	98 ± 0.9, Ir	5.0×10^4
Ir(III):Fe(II)	1:10	0.5	100 ± 0.9, Fe	99 ± 1.0, Ir	98 ± 1.0, Ir	4.2×10^4
	10:1		100 ± 0.6, Fe	98 ± 1.0, Ir	99 ± 1.0, Ir	4.1×10^4
Ir(III):Ag(I)	1:10	0.5	98 ± 1.1, Ag	100 ± 0.8, Ir	99 ± 1.0, Ir	4.1×10^4
	10:1		99 ± 1.0, Ag	99 ± 0.9, Ir	99 ± 1.1, Ir	4.9×10^4

Note: '±' refers to the standard deviation

*The aqueous phase was equilibrated twice with the equal volume of organic phase

[a] Ir(III) recovered using 0.1 mol L^{-1} thiourea solution in 1.0 mol L^{-1} $HClO_4$

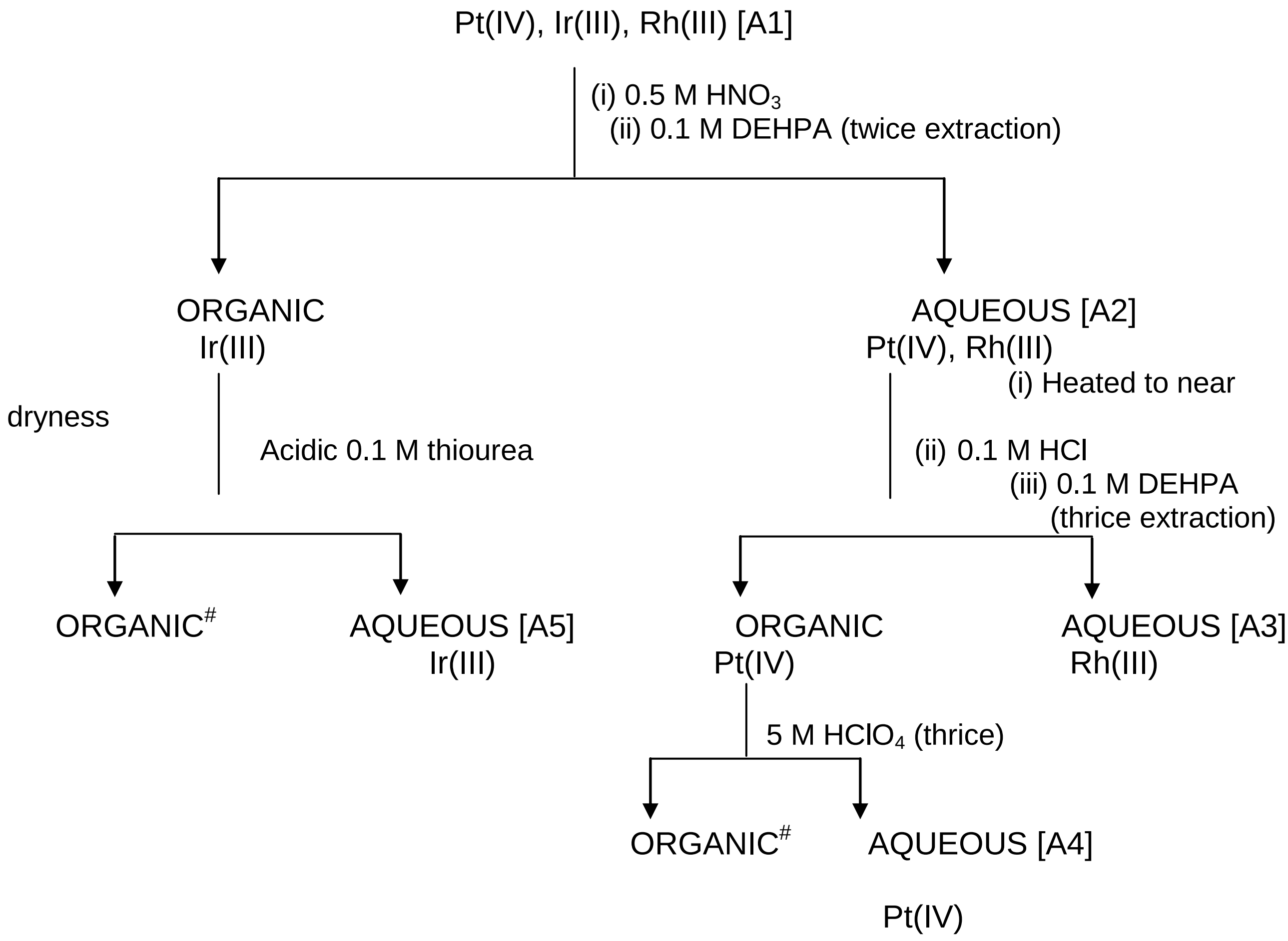
Recovery of platinum and rhodium from Pt-Rh thermocouple wire using DEHPA

The results of separation studies were successfully applied for the recovery of platinum and rhodium from Pt-Rh thermocouple wire. The digested solution of Pt-Rh thermocouple [T1] was used for the recovery of platinum and rhodium at 0.1 mol L^{-1} HCl (flowsheet 5.2). The solution [T1] was contacted thrice with equal volume of 0.1 mol L^{-1} DEHPA. Pt(IV) was quantitatively extracted while Rh(III) remained in the aqueous phase [T2]. The extracted Pt(IV) was scrubbed employing 5.0 mol L^{-1} $HClO_4$ [T3]. The composition of the solutions [T1], [T2] and [T3] are given in table 5.6.

Recovery of Pt(IV), Ir(III), Rh(III) and Pd(II) from synthetic mixture using DEHPA and Cyanex 923

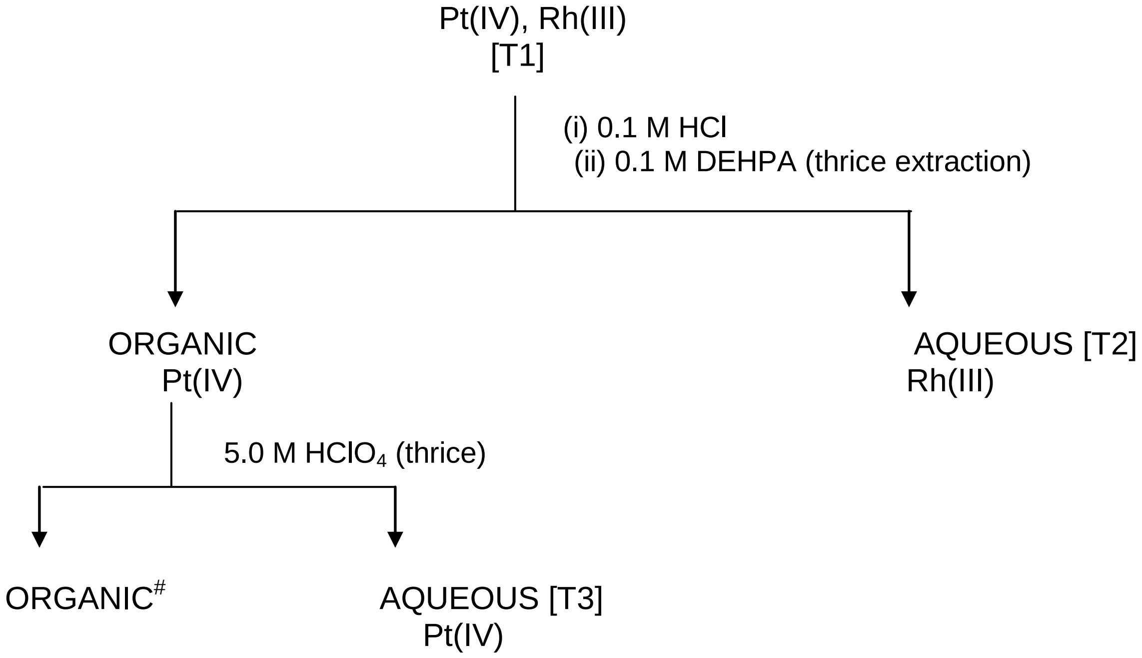
50 mL aliquot of an aqueous solution [A1] containing equimolar concentrations of Pt(IV), Ir(III), Rh(III) and Pd(II) at 0.50 mol L^{-1} HNO_3 was equilibrated twice with equal volume of 0.10 mol L^{-1} toluene solution of DEHPA. Ir(III) was extracted quantitatively into the organic phase leaving Pt(IV), Rh(III) and Pd(II) in the raffinate [A2]. The organic phase containing Ir(III) was treated with acidic 0.10 mol L^{-1} thiourea [A5] in order to back extract Ir(III). The raffinate [A2] containing Pt(IV), Rh(III) and Pd(II) was evaporated to near dryness. The residue was dissolved in HCl adjusting the final acidity to 0.10 mol L^{-1} HCl and final volume to 50 mL. The resulting solution was then equilibrated thrice with equal volume of 0.10 mol L^{-1} DEHPA to extract Pt(IV) while Rh(III) and Pd(II) remained in the aqueous phase [A3]. The extracted Pt(IV) was then recovered by equilibrating the loaded organic phase thrice with 5.0 mol L^{-1} $HClO_4$ [A4]. The aqueous solution [A3] was evaporated to near dryness with 2.0 mol L^{-1} HNO_3 and the final acidity was adjusted to 5.0 mol L^{-1} H_2SO_4. The resulting solution was equilibrated with 0.10 mol L^{-1}

Flowsheet 5.1: Recovery of PGMs from synthetic mixture using DEHPA



organic phase can be regenerated by washing with water

Flowsheet 5.2: Recovery of PGMs from thermocouple wire using DEHPA

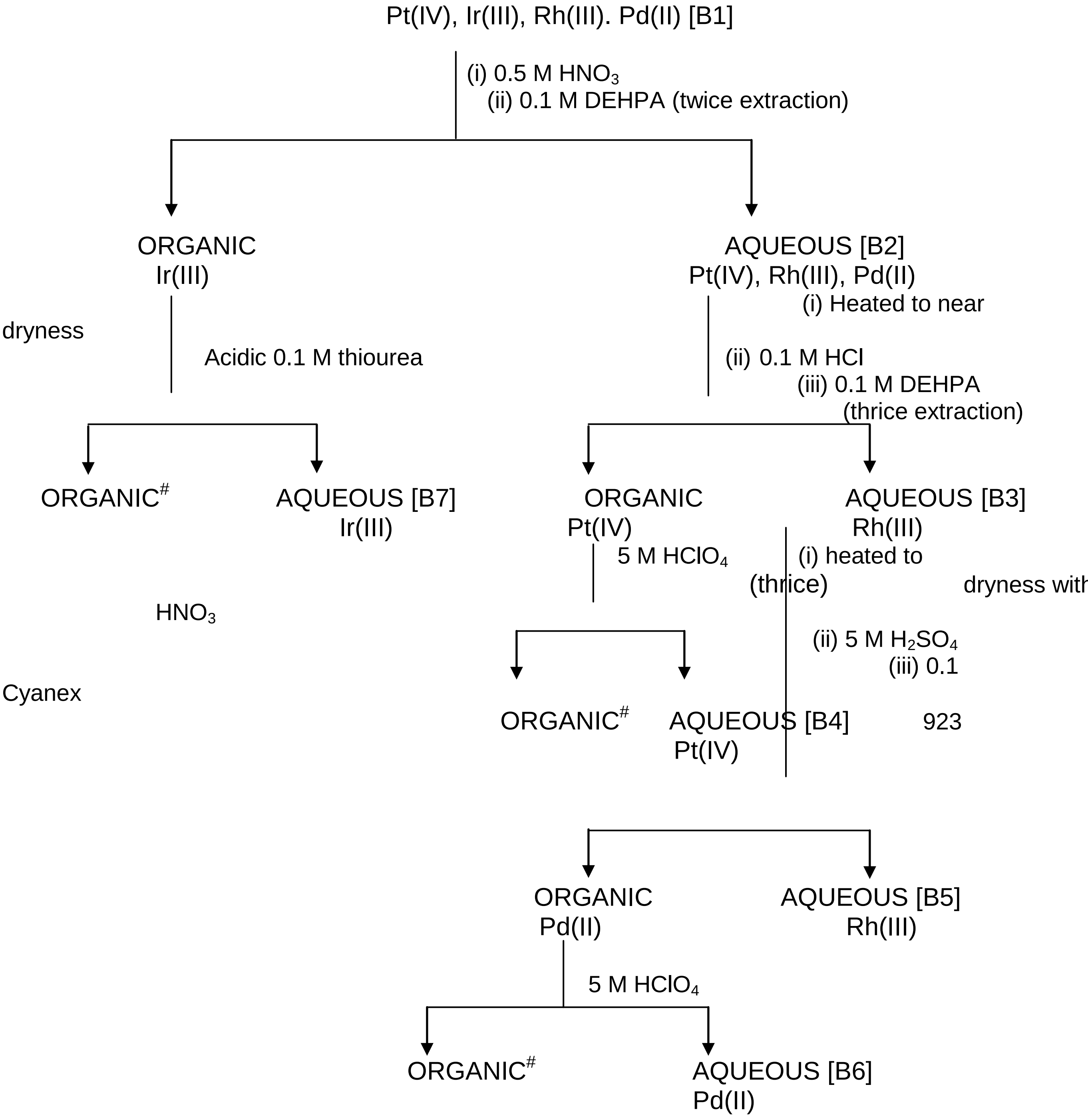


organic phase can be regenerated by washing with water.

Cyanex 923. This step resulted in quantitative transfer of Pd(II) into the organic phase while Rh(III) remained in the aqueous phase [A6]. The organic phase containing Pd(II) was scrubbed with 5.0 mol L^{-1} $HClO_4$ to recover Pd(II) [A7]. The concentration of the metal ions in the initial and the recovered solutions are given in table 5.7. The flowsheet 5.3 can be employed to separate and recover platinum, iridium, rhodium and palladium from real samples.

The data cited in this chapter reveal the potential of DEHPA for obtaining a variety of important binary separations involving Pt(IV)/Ir(III). The utility of the proposed separations has been successfully demonstrated by the recovery of pure platinum, iridium and rhodium.

Flowsheet 5.3: Recovery of PGMs from synthetic mixture using DEHPA and Cyanex 923



organic phase can be regenerated by washing with water

Table 5.5. Recovery of Pt(IV), Ir(III) and Rh(III) from a synthetic mixture using 0.1 mol L^{-1} DEHPA

Metal ions	Composition of initial solution [A1] (mg/l)	Composition of solution [A3] (mg/l)	Composition of solution [A4] (mg/l)	Composition of solution [A5] (mg/l)	Recovery (%)	Purity (%)
Pt	99.6 ± 1.7	<0.05	98.11 ± 1.7	<0.05	98.50	99.85
Ir	101.8 ± 2.1	<0.05	<0.05	102.2 ± 1.9	100	99.76
Rh	53.2 ± 1.1	54.1 ± 1.4	<0.1	<0.1	100	99.80

Note: '±' refers to the standard deviation
<0.05/<0.1 refers to less than the detection limit of the corresponding metal ion

Table 5.6. Recovery of Pt(IV) and Rh(III) from thermocouple wire using 0.1 mol L^{-1} DEHPA

Metal ions	Composition of initial solution [T1] (mg/l)	Composition of solution [T2] (mg/l)	Composition of solution [T3] (mg/l)	Recovery (%)	Purity (%)
Pt	6.73 ± 0.4	<0.05	6.56 ± 0.4	97.5	98.50
Rh	2.00 ± 0.2	2.09 ± 0.2	<0.1	100	97.66

Note: '±' refers to the standard deviation
<0.05/<0.1 refers to less than the detection limit of the corresponding metal ion

Table 5.7. Recovery of Pt(IV), Ir(III), Rh(III) and Pd(II) from a synthetic mixture using 0.1 mol L^{-1} DEHPA and 0.1 mol L^{-1} Cyanex 923

Metal ions	Composition of initial solution [B1] (mg/l)	Composition of solution [B4] (mg/l)	Composition of solution [B5] (mg/l)	Composition of solution [B6] (mg/l)	Composition of solution [B7] (mg/l)	Recovery (%)	Purity (%)
Pt	101.9 ± 1.5	101.5 ± 1.6	<0.05	<0.05	<0.05	99.61	99.80
Ir	102.4 ± 1.9	<0.05	<0.05	<0.05	102.1 ± 1.7	99.70	99.80
Rh	52.6 ± 1.0	<0.1	53.0 ± 1.1	<0.1	<0.1	100	99.71
Pd	54.1 ± 0.9	<0.05	<0.05	53.8 ± 0.9	<0.05	99.44	99.63

Note: '±' refers to the standard deviation

<0.05/<0.1 refers to less than the detection limit of the corresponding metal ion

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CONCLUSIONS

The present thesis describes studies on the extraction of Pt(IV), Ir(III), Rh(III), Ru(III) and Pd(II) and some associated metal ions namely Au(III), Fe(III), Cr(III), Al(III), Cu(II), Ni(II), Co(II), Fe(II) and Ag(I) in Cyanex 923, Cyanex 471X and DEHPA. The selected associated metal ions are likely to be encountered with PGMs in different real samples containing platinum metals. Some important characteristics of the different extraction systems have been identified by investigating the effect of equilibration time, temperature, nature of mineral acid and diluent and concentration of acid and extractant on the distribution of the metal ion. The extraction data have provided optimum conditions for achieving some binary separations involving Pt(IV), Ir(III), Rh(III) and Pd(II) and the associated metal ions. The information thus obtained has been utilized to develop schemes for the recovery of pure metal ions in good yields from some of the spent commercial samples.

The studies have projected Cyanex 923 to be useful for the separation and recovery of Pt(IV), Rh(III) and Pd(II) while Cyanex 471X and DEHPA for Pt(IV), Ir(III) and Rh(III). The detailed investigations on a particular PGM have been carried out from the medium exhibiting highest extraction of that platinum metal. With all the three extractants, under the specified experimental conditions, limiting extraction is attained with four to five minutes shaking suggesting that the kinetics of extraction is fast and may not pose any problem while scaling up the process. In all the cases phase separation is quicker and does not require the addition of any modifier. Apparently the author failed to observe any correlation between the nature of the diluents and the percent extraction. The study suggests that almost all the diluents under investigation show comparable extraction except chloroform in which very low extraction of palladium was observed. Thus a good spectrum of diluents is available to prepare the solution of the extractants. It is also apparent that for commercial purposes a cheaper diluent like kerosene can be usefully employed. The extraction of Pt(IV) in both the Cyanex extractants studied decreases with the increase in temperature indicating the process to be exothermic while in DEHPA the process was found to be endothermic. The extraction of Ir(III) in Cyanex 471X and DEHPA increases with the increase in temperature suggesting the process to be endothermic. The extraction of Pd(II) in Cyanex 923 was found to be exothermic. The results of slope analysis have been used to determine the extracting species. In the case of Cyanex 923 the stoichiometric ratio of metal:extractant is 1:2 for Pt(IV) and Pd(II) and the maximum loading obtained is 80 mM Pt(IV)/100 mM Pd(II) per 0.10 M extractant. The stoichiometric ratio with Cyanex 471X is 1:1 and 1:2 for Pt(IV) and Ir(III), respectively. The maximum loading obtained is 62 mM Pt(IV)/46 mM Ir(III) per 0.10 M Cyanex 471X. With DEHPA as an extractant the metal:extractant ratio in the extractaing species is 1:1 for both Pt(IV) and Ir(III) with a maximum loading of 54 mM Pt(IV) or 43 mM Ir(III) per 0.10 M DEHPA. The results of metal loading on extraction reveal that the extractants have a reasonably good loading capacity for the metal ions of interest.

Pt(IV), Ir(III) and Pd(II) are almost quantitatively extracted in one or more extractants in any one of the three mineral acids studied. This facilitates mutual separations of PGMs and a large number of their separations from the associated metal ions. A majority of separations have been achieved by selective extraction. However, in some cases selective stripping has been carried out. Invariably the stripping reagents used are such that they do not pose any serious problem in the subsequent processing of the metal ion solution. A number of binary separations with good separation factors have been achieved. In order to test the effectiveness of the separations, the metal ions have been taken in different mole ratios.

The conditions optimized for binary separations have been fused together to develop schemes for the recovery of platinum, iridium, rhodium and palladium in good yield and high purity from some representative matrices containing the said metals. Generally the recovery processes comprise of simple extraction and stripping steps. The steps involved are such that if a higher purity of the metal is desired the extraction/stripping cycle can be conveniently repeated. Cyanex 923 has proved to be a better extractant for Pt(IV) and Pd(II) whereas Cyanex 471X is a better option for Pt(IV) and Ir(III). However, DEHPA is found suitable for the recovery of Ir(III). The proposed separation methods have been successfully applied to some real samples namely catalyst standard, Pt-Rh thermocouple wire, coated ceramic honeycomb and palladium coated alumina catalyst for the recovery of platinum metals.

In order to assess the utility of the proposed methods on a commercial scale the hydrolytic stability and regeneration power of the extractants have been tested. All the three extractants are fairly stable towards long term acid contact and there is practically a negligible loss in the extraction efficiency of the extractants up to several cycles investigated.

To assess the potential of the selected organophosphorus extractants for their use as a mobile carrier, a representative study has been undertaken on the permeation of Pd(II) using Cyanex 923 impregnated flat sheet supported liquid membrane. The operational parameters were optimized for the rapid permeation of Pd(II). The liquid membrane technique containing Cyanex 923 as the carrier displayed an excellent recycling capacity and long term stability. The efficiency of the developed Cyanex 923-impregnated supported liquid membrane system was checked by applying it onto the synthetic mixture.

It should be noted here that the entire chemistry presented in the thesis has been carried out on a bench level. The scaling up of the procedures would invariably require some additional inputs. As far as the economics of the proposed methods is concerned it is difficult to draw any definite conclusion with the available data. However, factors like high loading capacity and good recycling property of the extractant and use of simple reagents for the recovery of metals suggest the economic viability of the suggested chemistry. It is important to mention that these extractants have been developed to recover platinum metals which are themselves very expensive and less abundant.

It is a little difficult to compare the efficacy of the proposed methods of separation on quantitative terms with those reported earlier. In the literature various extraction systems with different objectives in mind have been reported for the extraction of PGMs. A number of them have some definite advantages with some limitations. The high molecular weight amines and chelating agents used for the said purpose suffer from some drawback namely emulsion formation, high aqueous solubility and strict control of conditions. Out of the solvating organophosphorus extractants, TBP and TOPO lack selectivity and are more or less projected as universal extractants. As far as the studied extractants are concerned, poor aqueous solubility, miscibility with most of the commonly used diluents coupled with good loading and regeneration capacity speak in favour of the extractants studied.

Towards the end it may be pointed out that the metals taken up for the present investigation are of great industrial significance. The increasing applications of PGMs and less abundance of their natural sources have created a gap between the demand and supply of these metals. This necessitates the development of a strategy to recover them from spent and secondary sources. Continued efforts are being made to reuse the metal waste. The planning of the present thesis is such that it primarily focuses on this particular aspect of metal separation chemistry using commercial extractants. If after working out the desired parameters the proposed bench level chemistry is favourably scaled up it can be very useful in terms of economical savings and taking care of the problem of metal pollution. In no case the importance of various separations proposed herein, purely from the point of view of analytical chemistry, can be undermined.