EFFECT OF PROCESS VARIABLES ON THE KINETIC AND THERMODYNAMIC PARAMETERS OF PLATINUM SOLVENT EXTRACTION BY CYANEX 921

BY

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DECLARATION

I, **Ghislain Mutamba Kumwimba**, declare that the contents of this dissertation represent my own unaided work, and that the dissertation has not previously been submitted for academic examination towards any qualification. Furthermore, it represents my own opinions and not necessarily those of the Cape Peninsula University of Technology.

Signed Date

ABSTRACT

Platinum is a precious metal which may be processed under acidic conditions. Accordingly, the extraction of platinum from an acidic chloride media is of immense practical importance. In this study, the extraction of platinum was investigated in a *Pt(IV)-HCl-Cyanex 921* matrix in order to establish the effect of temperature, extractant concentration, pH and the initial platinum concentration which had been used in the evaluated solvent extraction (*SX*) process. The extractant phase contained a mixture of *Cyanex 92*1 and kerosene. In addition, the extraction mechanism of platinum, and the extracted species, are also described in the study, including the determination of the following: extraction ratio, extractant loading, distribution ratio, thermodynamic parameters, and the kinetic mechanism involved in the *Pt(IV)-HCl-Cyanex 921* system used. Inductively coupled plasma emission spectroscopy *(ICP-ES)* was used to measure the platinum concentration in the aqueous phase with a mass balance being used to determine the concentration of platinum in the organic phase.

Using a combination of the variables under investigation, the experiments which were evaluated indicated that it is possible to extract sufficient platinum chlorocomplex under the following conditions: pH of 1, *Cyanex 921* concentration of 8% (v/v), temperature of 298 K and an initial platinum concentration of 55.22 mg/L. Under these conditions the maximum organic-phase loading of 253.9 mg/L was achieved as compared to the theoretical loading of 507.24 mg/L. The equilibrium loading of ~50% of the platinum chlorocomplex in the organic phase was achieved after 2400 seconds of reactor operation. In this case, a distribution ratio of 9.4 was achieved. This value was observed to be higher as compared to the other *SX* conditions evaluated in this study.

The experimental data analysis was conducted with the aim of developing a regression model using a half-factorial experimental design of the order 2^4. This regression model was developed in order to be able to predict the distribution ratio for the experimental conditions used. A comparison between the experimental and the simulated results was carried out to determine whether the regression model was in agreement with the actual experimental data obtained. The mean absolute deviation between (*MAD*) the experimental and the simulated distribution ratio values was deduced to be 0.07 with an overall relative error of 1.74%; this indicated minimal deviation between the experimental and the predicted distribution ratio values. The sensitivity analysis performed in respect of the distribution ratio aided in both the evaluation of the overall *SX* process researched and its applicability. It was observed that the distribution ratio increased with an increase in the *Cyanex 921* concentration. This

phenomenon was attributed to an increase in the quantity of complexation sites and extractant concentration available in the organic phase during extraction. There was an insignificant decrease in the platinum distribution ratio (~3 to ~9%), with an increase in temperature for *SX* conditions with a pH of 1, while a 25% decrease was observed at a pH of 2. This substantial decrease was attributed to the decrease in the stability of the platinum chlorocomplex in the organic phase at a higher pH and temperature. In addition, the results suggest that half a mole of *Cyanex 921* participates in the stoichiometry reaction when a pH of 1 is used, while a quarter of a mole is involved when the pH is increased to 2.

Thermodynamic parameters, such as enthalpy ($\Delta H°$), entropy ($\Delta S°$) and Gibb's free energy ($\Delta G°$), including the activation energy (E_a), were also evaluated in order to determine the reaction dynamics of the *Pt(IV)-HCl-Cyanex 921 SX* process. The following results were achieved: the $\Delta H°$ was -5.92 to -0.85 kJ/mol while the $\Delta S°$ was -6.92 to 9.02 J/mol.K. Furthermore, $\Delta G°$ was determined to be -5.70 to -0.18 kJ/mol, while the E_a was found to be -3.44 to 1.76 kJ/mol. Under experimental conditions in which the loading capacity was at a maximum, the following thermodynamic parameters were determined as: $\Delta H°$ of -2.87 kJ/mol, $\Delta G°$ of -5.55 kJ/mol and $\Delta S°$ of 9.02 J/mol.K.

This meant that the process does not release excessive energy which, in turn, indicates its suitability for industrial application. On the other hand, the $\Delta S°$ reflected the affinity of the extractant towards platinum chlorocomplex, although some of experiments did indicate that a lower temperature positively influenced the extraction of the chlorocomplex into the organic phase. In addition, the negative $\Delta G°$ values obtained suggest the spontaneous nature of the solvation process. In view of the fact that the E_a was found to be < 20 kJ/mol, the process was classified as diffusion-controlled.

Overall, the low pH assisted in increasing the diffusive flux (J) of the platinum chlorocomplex into the organic phase with the forward mass transfer rate constant (δ_f) magnitude being 10^{-3} mm/s. Furthermore, the J of 2.2×10^{-7} mg/mm^2 s and the δ_f of 8.77×10^{-3} mm/s were achieve for conditions in which a maximum *KD* was achieved.

LIST OF OUTPUTS

The candidate has contributed the following to scientific development and knowledge during his candidacy (2008 to 2011):

International conference: oral and poster presentation

Kumwimba, G.K.M. and van der Plas, P.J. 2009. Optimisation of platinum solvent extraction from leach liquors. Mineral Processing Conference, 6-7th August 2009, Vineyard Hotel, Newlands, Cape Town, South Africa.

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NOMENCLATURE

Symbols	***Description***	***Units***
A	Interfacial area	[mm^{-1}]
A	Contact area between the two phases	[mm^2]
Ar	Arrhenius constant	-
B_w	Width	[mm]
C	Solute concentration	[mg/L]
D_i	Diameter	[mm]
D	Diffusion coefficient	[mm^2/s]
E_a	Activation energy	[kJ/mol]
H	Height	[mm]
J	Diffusive flux	[$mg/mm^2\ s$]
K_{ex}	Equilibrium reaction constant	M^{-1}
k	Rate constant	[mm/s]
KD	Distribution ratio	-
M	Mass	[g]
N	Number of stages	-
R	Universal gas constant	[J/mol.K]
V	Volume	mm^3
t	Time	[s]
T	Temperature	[K]
Y	Predicted response	-
$\Delta G°$	Standard Gibbs free energy	[kJ/mol]
$\Delta H°$	Standard enthalpy	[kJ/mol]
$\Delta S°$	Standard entropy	[J/mol.K]

Superscripts		**Subscripts**	
e	Equilibrium state	App	Apparent
i	Initial state	Aq	Aqueous phase
		Org	Organic phase
		f	Forward
		r	Reverse

Greek letters

β	Coefficient estimated from regression
δ_f	Forward mass transfer rate constant
α	Parameters defined by $\alpha = C_{aq}^{e} V_{aq} \big/ C_{org}^{e} V_{org}$

LIST OF ABBREVIATIONS

Abbreviations	**Descriptions**
ICP-ES	Inductively coupled plasma emission spectroscopy
SX	Solvent extraction
TOPO	Tri-n-octylphosphine oxide
% (v/v)	Percentage by volume
MAD	Mean absolute deviation
SLM	Supported liquid membrane

CHAPTER 1

INTRODUCTION

1.1 BACKGROUND

Platinum is an extremely important metal, not only in the manufacture of autocatalytic converters, but also for jewellery and, increasingly, for investment purposes. The increasing demand for platinum has rendered the recovery of this metal a strategic topic that has merited a great deal of attention during the last few decades (Jafarifar *et al*., 2005).

SX has been successfully applied in the extraction of platinum for a number of years. The demand for platinum has prompted research into the use and optimisation of the *SX* processes used to recover the metal (Brooks, 1991). The salient feature of the extraction chemistry of platinum involves the formation of chlorocomplexes in an acidic chloride solution. In addition, the different thermodynamic and process parameters applied in the recovery of the metal mean that there is considerable variation in the stability of the platinum chlorocomplexes in the *SX* processes evaluated (Chavan *et al*., 1998).

Generally, in hydrometallurgical processes, the platinum is leached using a solution of hydrochloric acid and chlorine gas, subsequent to the *SX* processes, in order to produce a refined metal of higher purity more quickly and at a low cost. The platinum in solution undergoes a conventional precipitation with wet chlorination (HCl/Cl_2) and a solution of ammonium chloride [NH_4Cl] so as to yield a precipitate of ammonium hexachloroplatinate [$(NH_4)_2PtCl_6$]. Thereafter, the precipitate recovered is calcined and reduced to a platinum sponge (Harris *et al.,* 1991).

In terms of *SX* processes, the selection of the extractant is one of the critical parameters which affects both the extraction of the high value metal and the overall process performance. This determines the commercial viability of the process to be evaluated. In platinum *SX*, several extractants have been used. *Cyanex 921* (better known as tri-n-octylphosphine oxide *(TOPO)*), the extractant researched in this thesis, is reported to have lower solubility and degradability in acidic solutions in comparison to other extractants, while its properties are suitable for use with aromatic diluents such as kerosene, toluene, etc. (Dziwinski and Szymanowski, 1998).

Kinetics and thermodynamic parameters are important in precious metal extraction. In certain cases, the application of theoretically developed kinetic and thermodynamic parameters tends to be unsuccessful when they are implemented in practice. It, thus, becomes important to investigate the platinum chlorocomplexes in different *SX* matrices so that the information obtained, both kinetic and thermodynamic, may be used to benefit the mining beneficiation industry. In this study, the influence of process conditions on kinetic and thermodynamic parameters, using a *Pt(IV)-HCl-Cyanex 921* in kerosene matrix, was evaluated.

1.2 RESEARCH STATEMENT

The work presented in this thesis concerns the extraction of platinum and includes the evaluation of solvation effects for parameters such as the temperature, pH, the concentration of the extractant and the initial platinum concentration. Furthermore, the thermodynamic parameters are quantified in order to evaluate both the spontaneity and mass transfer kinetics of the extraction process parameters not previously researched in low organic/aqueous phase ratio (*org/aq*) *SX* studies. It is hoped that this study will provide an insight into the influence of several thermodynamic and kinetic parameters on platinum *SX* in which low concentration of *Cyanex 921* was used as an extractant.

1.3 OBJECTIVES OF THE RESEARCH

The aim of this study was to determine the kinetic and thermodynamic parameters for a *SX* process in which a *Pt(IV)-HCl-Cyanex 921* matrix was used. Accordingly, the objectives of the study may be stated as follows:

- to investigate the influence of various parameters such as pH, temperature, extractant concentration, and initial platinum concentration on the platinum distribution ratio (*KD*);
- to determine the thermodynamic parameters, such as $\Delta H°$, $\Delta S°$ and $\Delta G°$, in order to predict the exothermicity and/or endothermicity of both the *SX* process and the affinity of the *Cyanex 921* in kerosene with regard to the platinum chlorocomplex as well as the spontaneity of the *SX* process, including the determination of E_a, so as to determine the mass transfer regime involved in this process;
- to evaluate kinetic parameters for the platinum chlorocomplex extraction using an appropriate *SX* mathematical model for the *Pt(IV)-HCl-Cyanex 921* in kerosene *SX* process evaluated. This includes the selection of an appropriate model for the evaluation.

1.4 RESEARCH QUESTIONS

- Will the *Cyanex 921* in kerosene be able to effectively extract a significant amount of platinum from a dilute solution of HCl?
- Will the parameters selected exert a significant influence on the extraction of platinum?
- Will the thermodynamic parameters be favourable in terms of the extraction of platinum into *Cyanex 921* in kerosene?

1.5 OUTLINE OF THE RESEARCH APPROACH USED

The following experimental approach was adopted in the study in order both to realise the objectives of the study and to enable the selection of an appropriate strategy with which to evaluate the kinetic and thermodynamic parameters for platinum extraction using low concentration of *Cyanex 921* in kerosene:

- to develop a factorial experimental design for the experiments to be conducted;
- to select appropriate process parameters to be varied in order to evaluate the extraction of platinum using *Cyanex 921* in kerosene;
- to establish which thermodynamic parameters must be monitored in order to evaluate their changes when process parameters such as pH are varied.

An extensive literature review was conducted on the topics of thermodynamic influences and kinetic parameter models for platinum *SX* using various extractants. This literature review included the evaluation of several aspects related to *SX* methodologies, with some being included in this thesis. The variables most likely to affect platinum extraction were identified and then used in order to realise the objectives as listed in section 1.3.

1.6 SCOPE AND DELIMITATION OF THE STUDY

Previous research into the thermodynamic and kinetic parameters for precious metal *SX* provided the basis for this study. In view of the wide scope of kinetic parameter modelling for the *SX* process, parameters such as pH, initial platinum concentration, extractant concentration and temperature were determined to be suitable for the purposes of this study and were, thus, the only parameters evaluated in the study. Much of the information which was considered to be of little relevance to the study has either been left out completely or only briefly described. This study focuses mainly on the platinum *SX* using low concentrations of *Cyanex 921* and refers to some of the other extractants that have been successfully used for the extraction of precious metals merely for comparative purposes.

As a result of the small volume of organic phase, the extraction of platinum with *Cyanex 921* in kerosene was studied in a batch reactor during the experimentation stage. The factorial experimental design methodology adopted was limited to important process parameters only.

CHAPTER 2

LITERATURE REVIEW

2.1 SOLVENT EXTRACTION

SX involves the distribution of different components between two immiscible phases, namely, the aqueous and the organic phases. *SX* has its origins in analytical chemistry in terms of which dilute aqueous solutions are concentrated using an extractant (Morrison and Freiser, 1957). The industrial application of *SX* was pioneered and developed in the 1940s for the recovery of uranium from ores and, later, for the treatment of waste from spent nuclear fuel (Cox, 2004). Nowadays, there are extensive industrial applications for *SX*. For example, *SX* is widely used in hydrometallurgy and is also a well established process for the recovery of metals such as transition elements, actinides and various precious metals (Cox, 1988).

Batch and continuous operational schemes may be used in *SX* operations. In terms of a batch process, the equipment used is a stirred tank, whereas devices such as mixer-settlers, columns and centrifugal contactors are used for continuous operations (Lo *et al.,* 1983). However, in *SX*, during the extraction process, metal ions are transferred to the organic phase with an extractant. The transfer is reversible and, thus, by changing both the chemical and the process conditions, it is possible to attain and to control the metal species transfer from the aqueous phase to the organic phase.

One of the most significant advantages of *SX* is that the specific complexation between the extractant and different metal ions permits the selective separation of the metals. Nevertheless, in spite of the positive aspects, there are some inherent drawbacks in *SX* systems. These drawbacks include the following: firstly, the reduction of the volume ratio between the organic phase and the aqueous phase as a result of solvent loss and, secondly, difficulties in phase separation (Suzuki and Matsunaga, 1991). In order to understand *SX* schemes, it is necessary to outline some of the principles of *SX*, that is, *SX* phase components, types of extracting reagents and the fundamental chemistry principles pertaining to *SX*.

2.2 ELEMENTARY PRINCIPLES OF *SX*

In general, the *SX* process comprises the following basic steps: extraction, scrubbing, stripping and regeneration. Figure 2.1 illustrates a typical *SX* circuit used in the platinum industry. The industrial steps involved in the *SX* process are explained in the subsections below.

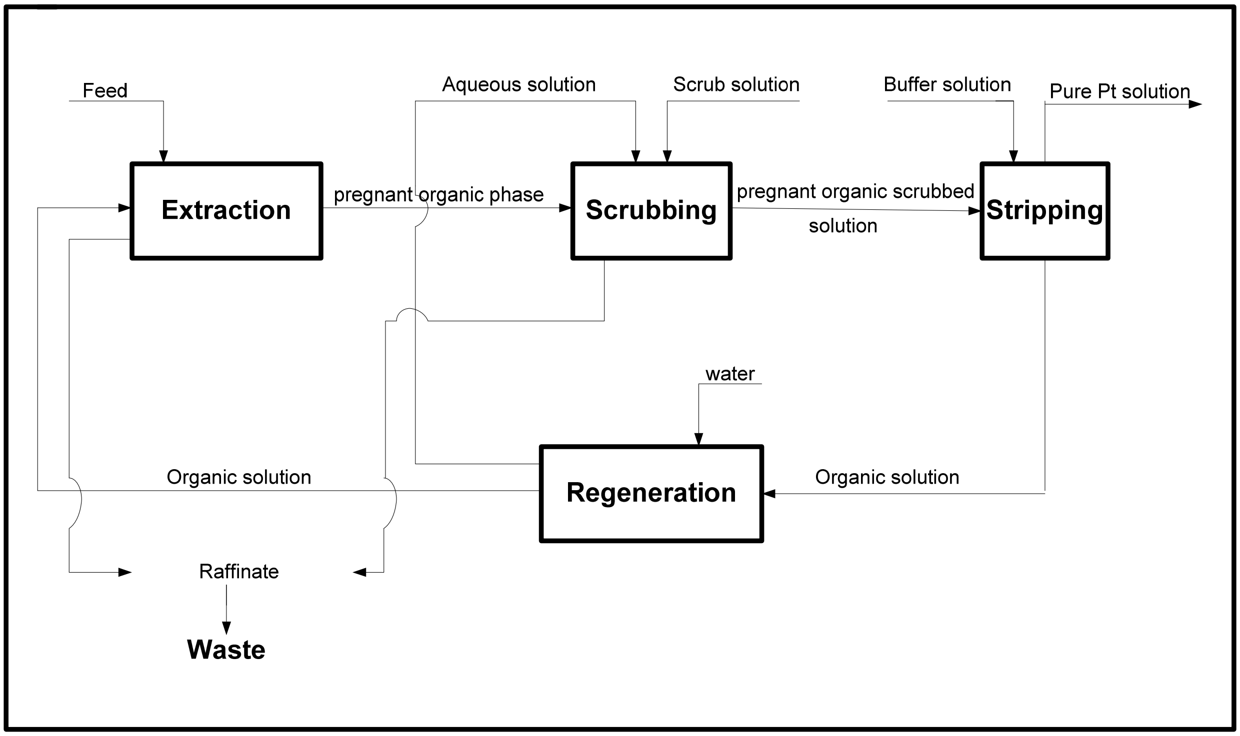

Figure 2. 1: A typical platinum *SX* circuit (Harris *et al*., 1991)

2.2.1 Extraction process

After leaching, the aqueous solution comes into contact with an organic phase which comprises an extractant in diluent with which to extract the metal into the organic solution. The pregnant organic phase is transferred to the scrubber while the raffinate is removed (Harris *et al*., 1991).

2.2.2 Scrubbing process

The pregnant organic phase is scrubbed with a clean scrubbing solution to remove the co-extracted impurities and acid. In general, the co-extracted impurities are removed using a 1 M scrubbing solution. The pregnant organic scrubbed solution containing the valuable metal of interest is transferred to the stripping process (Harris *et al.,* 1991; Lo *et al.,* 1983).

2.2.3 Stripping process

The pregnant organic scrubbed solution is stripped using a buffer solution (pH range of 2 to 5) at a temperature range of between 293 and 323 K in order to effect a selective recovery of the platinum for further processing (precipitation) while the organic solution is recovered for regeneration. Either an aqueous sodium acetate or sodium phosphate solution may be used as the buffer solution for stripping platinum from the pregnant organic phase. Platinum is usually stripped from the organic phase at a temperature range of between 313 and 323 K (Harris *et al*., 1991; Lo *et al.,* 1983).

2.2.4 Organic phase regeneration process

The organic solution is regenerated by washing it with water and transferring it to the extraction process while the aqueous solution is transferred back to the scrubbing process (Harris *et al.,* 1991; Lo *et al.,* 1983).

2.3 *SX* PHASE COMPONENTS

2.3.1 Aqueous phase component

The valuable component that has been extracted is normally either a metal ion or a metal ion complex in an aqueous solution. For extraction or stripping purposes, the aqueous phase pH may be adjusted so as either to decrease or to increase it by using inorganic salts or acids. The different extractable species may be categorised into the following four groups (Ritcey and Ashbrook, 1984):

- neutral metal species, e.g., $UO_2(NO_3)_2$;
- complex metal anions, e.g., $PtCl_6^{2-}, Cr(OH)_4^-$;
- complex metal cations, e.g., $[Ag(NH_3)_2]^+$ and $[Co(NH_3)_6]^{3+}; MoO_2^{2+}$;
- metal cations, e.g., $Zn^{2+}, Cu^+ \text{and } Fe^{2+}$.

2.3.2 Organic phase component

The organic phase comprises a solution containing both a lipophilic extractant and a diluent. During mixing, the formation of a third phase may also take place. The extractant forms complexes with the metal ions that are extracted from the aqueous solution. The fundamental element in the design of the *SX* process is the selection of a suitable extractant. This selection of the extractant depends upon both its selectivity and the mass transfer requirements necessary to achieve the desired solute recovery. It is essential that the following factors be taken into account when selecting a suitable extractant for a given extraction process (Gupta *et al.,* 1990; Blumberg, 1988; Barnes and Edwards, 1981):

- the capacity of the solvent to dissolve the solute in such a way that there is a high *KD* for the solute and a low *KD* for undesirable impurities;
- low solubility in the aqueous phase;
- low viscosity and sufficient density difference from the aqueous phase to avoid the formation of an emulsion;
- toxicity and flammability;
- the reactivity of the solvent towards the metal ion in the aqueous solution;
- large interfacial tension for the rapid coalescence of the dispersed solvent droplets;
- recoverability of the solvent from the raffinate;
- low corrosiveness of the solvent in respect of the common, low cost materials used in *SX* reactor construction.

2.3.2.1 Extractants used in SX applications

There are four main types of chemicals which may be used as metal extractants on the basis of their extraction chemistry and the metal species extracted (Sudderth and Kordosky, 1986). These extractants include anion and cation exchangers and chelators, including solvators or neutral extractants.

A. Anion exchangers

Anion exchangers are organic reagents that may easily form a salt in the organic phase while in contact with an aqueous acid solution (*HX*) according to Eq. 2.1.

$$\mathrm{B_{org} + HX_{aq} \leftrightarrow BH^{+}_{aq}X^{-}_{org}} \qquad \mathbf{2.1}$$

where B denotes the anion extractant.

By contacting the organic phase with an aqueous solution containing anionic metals species, $MX_{n}^{-(n-m)}$ *(n>m)*, an anion exchange process may occur. See Eq. 2.2 (Sudderth and Kordosky, 1986).

$$(n-m)BH^{+}X^{-}_{org} + MX_{n}^{-(n-m)}{}_{aq} \leftrightarrow \left(BH^{+}_{(n-m)}MX_{n}^{-(n-m)}\right)_{org} + (n-m)X^{-}_{aq} \qquad \textbf{2.2}$$

B. Cation exchangers

Organic acid *(HL)* based cation exchangers may extract metallic cations *(M^{+m})* according to the reaction in Eq. 2.3:

$$mHL_{org} + M^{-m}_{aq} \leftrightarrow ML_{m\ org} + mH^{+}_{aq} \qquad \textbf{2.3}$$

Eq. 2.3 above describes a cation exchange reaction in terms of which hydrogen ions are exchanged for the metal cation. Extractants which have been found to be useful in the extraction of metals using this mechanism include, *inter alia*, organic derivatives of phosphorous, monocarboxylic and sulfonic acids (Sudderth and Kordosky, 1986).

C. Chelators

The mechanism by which chelators are involved in *SX* are such that donor groups in the chelator form complexes with the metal ions. The equilibrium chemical reaction describing the metal extraction is the same as that reported for cation exchangers. Examples of these reagents include hydroxyoximes, derivatives of 8-hydroxyquinoline and β-diketones (Sudderth and Kordosky, 1986).

D. Neutral or solvating extractants

Solvating or neutral extractants *(S)* possess donor groups that do not contain dissociable protons and, because limited anionic or cationic groups are available in these extractants, the metal species are extracted from the aqueous phase as neutral complexes while the neutralising ion is a water soluble, negatively charged ligand *(X)*. The extraction reaction may be written in the form depicted in Eq. 2.4:

$$yS_{org} + M^{+m}_{aq} + mX^{-}_{aq} \leftrightarrow MXS_{y\ org} \qquad \textbf{2.4}$$

Solvating extractants are reagents which contain an oxygen-carbon bond. These extractants are ethers, esters, alcohols or ketones. Some extractants contain an oxygen or sulfur atom which is attached to a phosphorous molecule. Examples of solvating extractants include phosphoric esters, phosphine oxides and phosphine sulfides (Sudderth and Kordosky, 1986).

Cyanex 921 was the extractant used in this research. *Cyanex 921* is a solvating organic reagent which is widely accepted commercially in respect of metal recovery schemes. Its properties are outlined in Appendix A.1.

2.3.2.2 The application of diluents in *SX* processes

In *SX* processes, the term “diluent” refers to an organic liquid in which the extractant is dissolved. In general, the diluent forms part of the organic phase. Common diluents, such as aliphatic and naphthenic-aromatic mixtures, are used industrially (Ritcey and Ashbrook, 1984). Diluents have no capacity to extract metal ions from the aqueous phase although they may exert a considerable influence on the extraction, scrubbing, stripping and phase separation processes during *SX* (Gupta *et al.,* 1990). In other words, these diluents significantly affect both the physical properties of the organic phase, that is, density and viscosity, as well as the interfacial phenomena between the organic and aqueous phases including the extraction equilibrium, selectivity and extraction kinetics of the *SX* process (Mohapatra *et al.*, 2007).

According to Mohapatra *et al.* (2007), a variety of interactions occur between the diluent and the extractant. These include dipole-dipole, pi-electron interactions and hydrogen bonding. The selection of the diluent may be based on its flash point, on minimising evaporation loss and the risk of fire; viscosity and environmental considerations (Lo *et al.,* 1983). Both naphthenic and aromatic diluents influence both the loading capacity of the extraction solution and the solubility of the metal complex. Some of the diluents used in *SX* processes include kerosene, toluene, and commercial extractants such as Kerosol 200, Shellsol 2325, etc.

As a result of its availability in South Africa and its suitable properties, kerosene was selected as the appropriate diluent for use in this study (see properties in Appendix A.2). Generally, aliphatic hydrocarbons have a higher extraction coefficient than aromatic hydrocarbons. Kerosene is obtained from petroleum distillation and it contains paraffinic hydrocarbons with limited aromatic and naphthenic hydrocarbons (Ritcey and Ashbrook, 1984).

2.4 CHEMISTRY OF PLATINUM *SX* PROCESSES

2.4.1 Formulation of chlorocomplexes

Platinum forms complexes with a variety of different ligands. The platinum species encountered in chloride media are depicted in Table 2.1 (Grant, 1990; Warshawsky, 1987). Platinum forms a significant portion of complex, multi-nuclear species. In a chloride media, the hexachlorocomplex anion predominantly forms a tetravalent oxidation state (Bernadis *et al*., 2005). The platinum may be precipitated from an aqueous chloride solution as an ammonium-based salt - see Eq. 2.5. As a result, the selective precipitation of the tetravalent form of the platinum complex becomes possible.

$$2NH_4Cl + PtCl_6^{2-} \leftrightarrow (NH_4)_2PtCl_6 + 2Cl^- \qquad \textbf{2.5}$$

Table 2.1: Platinum species and complexes found in various media

Platinum species	*Platinum chlorocomplex*
$Pt(II)$	$PtCl_4^{2-}$
$Pt(IV)$	$PtCl_6^{2-}$

2.4.2 Ligand substitution reactions in platinum *SX* processes

As a result of the differences in the ligand substitution kinetics involved, the platinum metal-chlorocomplex is, in general, less reactive than those of other base metals. The reactivity of platinum depends on both its oxidation state and on the nature of its ligands. The order of reactivity with a soft donor ligand is directly related to the platinum periodicity. Metals with a divalent oxidation state are readily susceptible to substitution by soft donor ligands and the rates of substitution may be several orders of magnitude faster than for metals with higher oxidation states (Bernadis *et al*., 2005).

2.4.3 Platinum based ion-exchange reactions

The platinum metal-chlorocomplexes depicted in Table 2.1 occur in an acidic chloride solution and are anionic. They are, therefore, capable of undergoing anion-exchange reactions with a variety of organic bases *(B)* - see Eq. 2.6:

$$nB^{+}Cl^{-} + PtCl_6^{n-} \leftrightarrow B_nPtCl_6 + nCl^{-} \qquad \textbf{2.6}$$

In platinum extraction, several kinetic factors, such as forward diffusion rate constant and *J*, tend to influence extraction reactions. In addition, it is also imperative to consider the thermodynamic parameters. It is essential that the *SX* processes used to recover platinum be suitable for a wide range of complexes in different oxidation states which may, in turn, affect the kinetic and thermodynamic stability of the chlorocomplex during the extraction process (Cox, 1992).

2.5 MATHEMATICAL ANALYSIS OF *SX* PROCESSES

2.5.1 Loading of the extractant

Both the loading mechanism and the overall capacity of the extractant are important in terms of its commercial applicability and viability. The overall capacity of the extractant provides the maximum concentration of the solute ions which may be extracted from the aqueous phase into the organic phase at a constant temperature and pH (Sekine and Hasegawa, 1977). In general, it is advisable to operate under optimum solute loading conditions. A modifier may be added to the organic phase in order to increase the solubility of the metal to be extracted (Kumar *et al.*, 2008). Furthermore, the capacity of the extractant to provide sufficient loading sites may be determined by contacting a solvent several times with a fresh aqueous solution until the most favourable loading has been achieved (Ritcey and Ashbrook, 1984). See Eq. 2.7 below for a description of the mass balance of the solute at equilibrium in *SX* process:

$$V_{aq}C_{aq}^{e} + V_{org}C_{org}^{e} = V_{aq}C_{aq}^{I} \qquad \textbf{2.7}$$

The loading of the solute may be expressed in terms of the following equation (Gupta *et al.,* 1990):

$$\text{Loading} = \frac{V_{aq}}{V_{org}}\left(C_{aq}^{I} - C_{aq}^{e}\right) \qquad \textbf{2.8}$$

where V_{aq} and V_{org} denote the volumes of the aqueous and aqueous phases, respectively, *C* refers to the solute concentration, and the superscripts *I* and *e* refer to the initial and equilibrium states, respectively. The loading capacity corresponds to the maximum platinum concentration *(mg/L)* that may be loaded onto the organic phase for a given extractant concentration, irrespective of the platinum concentration in the aqueous phase.

2.5.2 Distribution ratio

SX is controlled by the following two important factors, namely, the *KD* and metal selectivity (Lo *et al.,* 1983). At equilibrium in dilute solutions, the ratio of the solute concentration in the organic and aqueous phase is known as the *KD* of the solute (Cox *et al.,* 1992) - see Eq. 2.9 below:

$$\mathrm{KD} = \frac{\mathrm{C}^{\mathrm{e}}_{\mathrm{org}}}{\mathrm{C}^{\mathrm{e}}_{\mathrm{aq}}} \qquad \textbf{2.9}$$

where $\mathrm{C}^{\mathrm{e}}_{\mathrm{org}} = \frac{\mathrm{V}_{\mathrm{aq}}}{\mathrm{V}_{\mathrm{org}}}\left(\mathrm{C}^{\mathrm{I}}_{\mathrm{aq}} - \mathrm{C}^{\mathrm{e}}_{\mathrm{aq}}\right)$ **2.10**

Eq. 2.10 represents a mass balance expression of the solute (platinum chlorocomplex) at equilibrium. Accordingly, Eq. 2.9 may be rearranged as follows:

$$\mathrm{KD} = \frac{\frac{\mathrm{V}_{\mathrm{aq}}}{\mathrm{V}_{\mathrm{org}}}\left(\mathrm{C}^{\mathrm{I}}_{\mathrm{aq}} - \mathrm{C}^{\mathrm{e}}_{\mathrm{aq}}\right)}{\mathrm{C}^{\mathrm{e}}_{\mathrm{aq}}} \qquad \textbf{2.11}$$

where *KD* is referred to as the distribution ratio.

It is preferable for the *KD* to be greater than unity (*KD > 1*) as a large ratio value implies that the majority of the metal is concentrated in the organic phase and a lesser amount of solvent is required for the recovery. The extraction percentage may be expected to be high when a low value of aqueous/organic volumetric ratio is used. Nevertheless, the organic and aqueous ratio of the phases in a mixer has a considerable effect on entrainment. Once the *Or/Aq* is greater than unity, it is desirable to disperse the minority liquid in order to minimise back mixing (Treybal, 1963). Finally, the extraction ratio may be represented by Eq. 2.12 below:

$$\text{Extraction ratio} = \frac{[\mathrm{C}_{\mathrm{t}}]_{\mathrm{org}}}{[\mathrm{C}_{\mathrm{i}}]_{\mathrm{aq}}} \qquad \textbf{2.12}$$

where the subscript *i* and *t* denote the initial and final states, while *C* refers to the solute concentration.

In accordance with previous conventions, it is easy to determine the mass of the solute remaining in the aqueous phase after a number *(n)* of extraction stages - see Eq. 2.13 (Cox *et al.,* 1992).

$$M_{aq} = M_{aq(1)}\left[\frac{1}{\left(1 + KD\frac{V_{aq}}{V_{org}}\right)}\right]^{n} \qquad \textbf{2.13}$$

where $M_{aq(1)}$ is the initial mass of the solute in the aqueous phase.

2.5.3 Suggested platinum *SX* mechanism using *Cyanex 921*

Over the years, a number of possible mechanisms have been suggested for the extraction of platinum chlorocomplex with *Cyanex 921* as a solvating reagent. The metal to be extracted from the acidic aqueous solution was in the form of $PtCl_6^{2-}{}_{(aq)}$. The stoichiometric equation, that is, Eq. 2.14, was suggested in order to describe the interaction of *Cyanex 921* in kerosene and $PtCl_6^{2-}{}_{(aq)}$ in an acidic solution. This model is similar to the models developed by Mhaske and Dhadke (2001a), Martinez *et al*. (1997) and El-Dessouky *et al.* (2008).

$$PtCl_6^{2-}{}_{(aq)} + mH^{+}{}_{(aq)} + yTOPO_{(org)} \xleftrightarrow{K_{ex}} H_mPtCl_6.\,y[TOPO]_{(org)} \qquad \textbf{2.14}$$

Where K_{ex} denotes the equilibrium reaction constant which is defined as a ratio of both the forward (k_f) and the reverse rate constants (k_r) at equilibrium, respectively. This is discussed in chapter 3 (mathematical model chapter). The equilibrium as described in Eq. 2.14 may be represented by:

$$K_{ex} = \frac{KD}{\left[H^{+}\right]^{m}\left[TOPO\right]^{y}} \qquad \textbf{2.15}$$

where KD is equivalent to $\left[H_m PtCl_6(TOPO)_y\right] / \left[PtCl_6^{2-}\right]$ as described in Eq. 2.9. If the logarithm of Eq. 2.15 is rearranged the result is Eq. 2.16;

$$\log \mathrm{KD} = \log \mathrm{K}_{\mathrm{ex}} - \mathrm{m}\log\left[\mathrm{H}^{+}\right] - \mathrm{y}\log\left[\mathrm{TOPO}\right] \qquad \mathbf{2.16}$$

Eq. 2.16 may be simplified to obtain Eq. 2.17.

$$\log \mathrm{KD} = \log \mathrm{K}_{\mathrm{ex}} + \mathrm{C} \qquad \mathbf{2.17}$$

where the constant, *C*, is equivalent to -*(m log [H$^+$] + y log [TOPO])* for individual experiments.

2.5.4 Thermodynamic effects in *SX* processes

The thermodynamic characteristics, such as Δ*H*°, Δ*S*° and Δ*G*°, all play a significant role in *SX* processes. Δ*H*° may be calculated from the van’t Hoff equation as follows (Kumar *et al.*, 2008; Mohapatra *et al.*, 2007; Duche and Dhadke, 2001; Potapov *et al.*, 2001):

$$\log \mathrm{KD} = -\frac{\Delta \mathrm{H}^{\circ}}{2.303\mathrm{RT}} + \mathrm{C}_{\mathrm{int.}} \qquad \mathbf{2.18}$$

where *R* is the gas law constant, *T* is the temperature at which the *SX* process is run, and C_{int} is an integration constant which includes the equilibrium reaction constant, the activity and the activity coefficient for other components (reagents) which are assumed to be constant under defined experimental conditions. The corresponding Δ*G*° can be calculated by using Eq. 2.19.

$$\Delta \mathrm{G}^{\circ} = -2.303\mathrm{RT}\log\mathrm{KD} \qquad \mathbf{2.19}$$

In addition, the relationship between Δ*S*°, Δ*H*°, Δ*G*° and temperature may be represented by Eq. 2.20 (Ebbing, 1993).

$$\Delta \mathrm{G}^{\circ} = \Delta \mathrm{H}^{\circ} - \mathrm{T}\Delta \mathrm{S}^{\circ} \qquad \mathbf{2.20}$$

Similarly, taking into account Eq.(s) 2.19 and 2.20, Eq. 2.18 may be written as *log KD* = $\Delta H^{\circ}/2.303RT$ + $\Delta S^{\circ}/2.303R$. Accordingly, the values of ΔH° and ΔS° may be obtained from the slope and intercept of the linear regression of the *log KD* against the reciprocal of absolute temperature, *(1/T)*. From this, it is possible to characterise several thermodynamic states. These are presented in Table 2.2.

Table 2.2: Description of quantified thermodynamic parameters (Ebbing, 1993)

Evaluated parameter(s)	***Description***
$\Delta H^{\circ} < 0$	Exothermic reaction
$\Delta H^{\circ} > 0$	Endothermic reaction
$\Delta S^{\circ} > \Delta H^{\circ}/T$	Spontaneous reaction
$\Delta H^{\circ} - T\Delta S^{\circ} < 0$	Spontaneous reaction (left to right)
$\Delta H^{\circ} - T\Delta S^{\circ} > 0$	Non-spontaneous reaction (left to right); spontaneous in the opposite direction (right to left)
$\Delta H^{\circ} - T\Delta S^{\circ} = 0$	The reaction is at equilibrium

Overall, the following conditions may be useful in judging the spontaneity of a reaction with known thermodynamic parameters (Ebbing, 1993):

- when ΔG° is a large negative number (<< -10 kJ/mol), the reaction is spontaneous (left to right) and the reactants transform almost entirely to products when equilibrium is reached;
- when ΔG° is a large positive number (>> 10 kJ/mol) the reaction is non-spontaneous (left to right) and the conversion of reactants to products will be minimal at equilibrium;
- when ΔG° has either a small negative or positive value (> -10 to < 10 kJ/mol), the reaction gives an equilibrium mixture with significant amounts of both reactants and products.

Furthermore, if the above information (Table 2.2) is taken into account and if the signs of the two terms on the right side of Eq. 2.20 are examined, it is possible to distinguish the following four separate cases (Ebbing, 1993):

- when ΔS° is positive and ΔH° is negative, a process is spontaneous;

- when ΔS° is positive and ΔH° is negative, a process is spontaneous at high temperatures with exothermicity playing a small role in the balance;
- when ΔS° is negative and ΔH° is negative, a process is spontaneous at low temperatures with exothermicity playing an extremely important role;
- when ΔS° is negative and ΔH° is positive, a process is not spontaneous at any temperature, despite the fact that the reverse process is spontaneous.

In general cases, thermodynamic parameters are used in *SX* research in order to evaluate the reaction dynamics of the constituents involved in the process including the determination of reaction spontaneity, heat generation from the process and the affinity of the extract towards the metal of interest.

2.6 FACTORS INFLUENCING *SX* PROCESSES

In order to develop a recovery process for the platinum chlorocomplex from the bulk acidic aqueous solution into *Cyanex 921* in kerosene, it is necessary to discuss the following factors: temperature, extractant concentration, pH and initial platinum concentration. These factors were all identified as having an influence on *SX* processes.

2.6.1 Effect of temperature on *SX* processes

The effect of temperature is the most complex factor affecting the equilibrium state in platinum extraction processes. An increase in temperature may increase the extraction of the chlorocomplex as a result of the increased dehydration of the species. On the other hand, an increase in temperature may decrease the extraction rate as a result of the decreased stability of the complex at high temperatures (Kumar *et al.*, 2008). Based on thermodynamic principles, an increase in the temperature may also lower the viscosity of organic solvents. In addition, an increase in temperature may enhance the solvating capacity of the extractant. Quantitatively, the relationship between the rate at which the reaction proceeds and its temperature may be determined by the Arrhenius equation. At higher temperatures, the probability that two molecules will collide is higher. This higher collision rate results in a higher kinetic energy which, in turn, has a positive effect on the E_a of the reaction (Moore, 1962; Levenspiel, 1999). Another method of determining temperature dependency is to ascertain whether the reaction is either exothermic or endothermic (see Table 2.2 highlighted in section 2.5.4).

Accordingly, the effect of temperature on reaction rates may be represented by the Arrhenius equation in linearised form as follows:

$$\ln \mathrm{k} = \frac{\mathrm{E_a}}{\mathrm{RT}} + \ln \mathrm{A_r} \qquad \mathbf{2.21}$$

where A_r refers to the Arrhenius constant, E_a is the activation energy, R is the gas constant, T denotes the temperature and k is the reaction rate constant. Alternatively, at the same concentration, the E_a values may be obtained from the Arrhenius equation by using the forward k_f and reverse k_r rate constant values at different temperatures (Levenspiel, 1999). In this case Eq. 2.21 becomes:

$$\ln \frac{\mathrm{k_f}}{\mathrm{k_r}} = \frac{\mathrm{E_a}}{\mathrm{R}}\left(\frac{1}{\mathrm{T_1}} - \frac{1}{\mathrm{T_2}}\right) \qquad \mathbf{2.22}$$

In this thesis, instead of using Eq. 2.21 and/or 2.22, the forward reaction rate constant for a temperature-dependent, reaction was treated with the activation complex theory for the estimation of E_a as shown in Eq. 2.23 (Baruah and Khare, 2007).

$$\mathrm{E_a} = \Delta \mathrm{H}^{\circ} + \mathrm{RT} \qquad \mathbf{2.23}$$

In addition, Zhen-ning *et al.* (2010) state that the rate-determining or controlling step for a *SX* process will be the diffusion of the chlorocomplex when the E_a is < 20 kJ/mol while, at the same time, the process will be controlled by the concentration of the extraction reagents when the E_a is > 40 kJ/mol. Furthermore, if the E_a is between 20 to 40 kJ/mol, both the complexation reaction and the diffusion of the metal to be extracted through the aqueous-organic laminar film will contribute to the rate-determining step for the *SX* process. Therefore, by estimating the E_a for the *SX* process, it is possible to determine the mass transfer regime.

2.6.2 Effect of extraction reagents concentration

Collision theory predicts that the frequency of collisions between two reactants increases when the concentration of the reactants increases (Murry and Fay, 1995). Accordingly, a lesser concentration of any of the reactants will result in fewer collisions, and the reaction will probably happen at a slower rate. However, the rate of reaction is limited by the concentration of the diluted solution or reactant and any increase in the concentration of the other reactant will not make any difference. It is, thus, desirable that the concentration of one of the reactants be in excess so as to enable an increase in the concentration of the other constituents in order to produce an increase in the rate of the reaction (Moore, 1983, Mhaske and Dhadke, 2001b).

2.6.3 Effect of pH

The extraction of precious chlorocomplexes and the formation of a solvation mechanism are influenced by the pH of the aqueous phase (Kumar *et al.,* 2008; El-Dessouky *et al*., 2008). The platinum chlorocomplex ions may exist in the aqueous phase in different ionic forms including $PtCl_6^{2-}$ and $PtCl_4^{2-}$, as indicated previously. The concentration of platinum chlorocomplexes and the process pH may dictate which particular platinum chlorocomplex species will be predominant in the aqueous phase. $PtCl_6^{2-}$ anions dominate in acidic aqueous solutions as an extractable species in comparison to $PtCl_4^{2-}$ (Kumar *et al.,* 2008). This proves that the mechanism of extraction of platinum chlorocomplex ion is pH dependent and that pH may affect the stability of the metal of interest in the organic phase and, thus, influence the extraction kinetics of various complexes by competing with the platinum chlorocomplex during solvation.

2.6.4 Behaviour of *Cyanex 921* in different *SX* matrices

Table 2.3 represents an overview of some extraction matrices, diluents, molar participation of H^+ and *Cyanex 921* including thermodynamic parameters in which *Cyanex 921* was involved. It is noticed that a range of 0.05-0.3 mol/L of *Cyanex 921* concentration was used successfully in the extraction of Zn(II) with an extraction efficiency of 96%. For this study, the reported average K_{ex} was 14 M^{-3} for which two moles of *Cyanex 921* and one mole of H^+ were involved in the extraction of Zn(II) between the temperature range of 283-323 K. The slope analysis revealed the formation of $HZnCl_3$.2*Cyanex 921* in the organic phase (El-Dessouky *et al.*, 2008).

Furthermore, it was reported that *Cyanex 921* was found to be a better extractant for platinum *SX* processes (Mhaske and Dhadke, 2001b). In this study by Mhaske and Dhadke (2001b), the extraction of platinum using *Cyanex 921* in toluene investigated at equal volumes of organic and aqueous phase with *Cyanex 921* concentration range of 0.08-0.52 mol/L was such that four moles of *Cyanex 921* and two moles of H^+*,* respectively, were involved during the extraction process. In addition, it was reported that in the temperature range of 283-333 K, the process was moderately exothermic (~-15 kJ/mol). In this study, the suggested stoichiometric equation for the extraction was H^+.2(*Cyanex 921*)$_2$$PtCl_6^{2-}$.

The *SX* of Cu(II) from a hydrochloric acid solution was investigated using a *Cyanex 921* concentration range of 0.05-0.5 mol/L in kerosene organic phase while the organic and aqueous phases were equal with a temperature range of 300-333 K . It emerged from the results that two moles of *Cyanex 921* and 2 moles of H^+ participated in the extraction of Cu(II). This, in turn, suggests that a H_2CuCl_4.2*Cyanex 921* molecule was formed. Similar to the *Pt(IV)-HCl-Cyanex 921* matrix, negative $\Delta H°$ values were obtained. The latter suggests that the extraction process was exothermic while negative $\Delta S°$ values would indicate that the reaction was spontaneous over a wide range of temperatures (Mishra and Devi, 2011). From these *SX* studies highlighted above, it is clear that the stoichiometric mechanism of a *Pt(IV)-HCl-Cyanex 921* matrix may change depending on the process parameters used. The *SX* studies highlighted in Table 2.3, indicate that the ratio of the organic and the aqueous phase was maintained at 1:1. For this study, a low organic to aqueous phase ratio was used, i.e., 1:9.

Table 2.3: Representation of extraction matrices, diluents, slopes and thermodynamic aspects for metal ion extractions by *Cyanex 921*

Reference	***Mishra and Devi, 2011***	***El-Dessouky et al., 2008***	***Mhaske and Dhadke, 2001b***
Matrix	Cu(II)-HCl-*Cyanex 921*	Zn(II)-HCl-*Cyanex 921*	Pt(IV)-HCl-*Cyanex 921*
Diluent	Kerosene	Kerosene	Toluene
% Extraction	n/d	96%	n/d
Slope log *KD*/log *[Cyanex 921]*	2	2	4
Slope log *KD*/log $[H^+]$	2	1	2
$\Delta G°$	n/d	n/d	n/d
$\Delta H°$	-12.7 kJ/mol	n/d	-15.73 kJ/mol
$\Delta S°$	-10.4 J/K.mol	n/d	n/d
K_{ex}	n/d	24 M^{-3}	n/d
(Org/Aq) ratio	1:1	1:1	1:1
Temperature range	300-333 K	288-323 K	283-333 K
Cyanex 921 concentration	0.05-0.5 mol/L	0.05-0.3 mol/L	0.08-0.52 mol/L

n/d: numerical value(s) not determined/quantified

Table 2.3: Cont.

Reference	***Mhaske and Dhadke, 2001a***	***Mhaske and Dhadke, 2002***	****Parameters for this study***
Matrix	Rh-Pt-Pd-HCl-*Cyanex 921*	Os-Ru-Ir-Cyanex 921	Pt(IV)-HCl-*Cyanex 921*
Diluent	Toluene	Toluene	Kerosene
% Extraction	~98%	55-99%	-
Slope log *KD*/log *[Cyanex 921]*	n/d	n/d	-
Slope log *KD*/log $[H^+]$	n/d	n/d	-
$\Delta G°$	n/d	n/d	-
$\Delta H°$	n/d	n/d	-
$\Delta S°$	n/d	n/d	-
K_{ex}	n/d	n/d	-
Ratio (org/aq)	1:1	1:1	1:9
Temperature range used	303 K	303 K	298-318 K
Cyanex 921 concentration	0.001-0.1 mol/L	0.0005-0.1 mol/L	0.046-0.18 mol/L

n/d: numerical value(s) not determined/quantified

**see section 4.4*

2.7 SUMMARY

This chapter discusses general information on the *SX* process and the flow diagram of the extraction of platinum. In terms of chemistry, platinum forms complexes with a variety of different ligands and the chemistry is extremely complex. Different diluents and the extraction mechanism are emphasised. The mathematical analysis of *SX* is presented. This includes the *KD*, loading of solute onto organic phase and also the influence of thermodynamic parameters ($\Delta H°$, $\Delta S°$ and $\Delta G°$). The stoichiometric reaction (Eq. 2.14) is presented in order to understand the extraction mechanism of platinum chlorocomplex as reported in numerous literature studies. The effect of factors such as temperature, pH and the reagent concentration on *SX* are also discussed.

CHAPTER 3

MATHEMATICAL MODELS (THEORY)

3.1 INTRODUCTION

This chapter discusses the mathematical models used in the evaluation of kinetic parameters for *SX* processes using experimental data. The aim of these mathematical models is to determine the *SX* reaction constants so as to be able to evaluate the E_a, in order to determine the controlling step (kinetic regime) of the *SX* process presented in this thesis. Generally, the extraction process consists of a series of steps including: 1) the transfer of a metallic complex ion from the aqueous phase to the interface, 2) the transfer of the ions to the organic phase, and 3) the transfer of the products away from the interface. In *SX*, the viscosity of the two phases, the intensity of agitation, the temperature, pH, metal concentration, and extractant concentration, are all factors that may influence the extraction rates.

3.2 MODEL ASSUMPTIONS

The following assumptions were considered during the selection of a simple model for platinum *SX* using *Cyanex 921* in kerosene:

- isothermal conditions during individual extraction experiments as the experiments were conducted in a controlled temperature environment;
- the two distinct liquid phases are prevalent, that is, the aqueous phase containing the metal of interest and the organic phase (*Cyanex 921* and diluent), are assumed to be prevalent during extraction;
- the extraction reaction is assumed to be reversible while the interfacial contact area is assumed to be constant during the extraction;
- the mass-transfer process is treated formally as a pseudo-first-order reversible reaction with respect to the metal cation.

3.3 *SX* RATES AND MASS TRANSFER CONTROLLING MECHANISMS

In *SX*, the rate of extraction is normally controlled by the slowest step which influences the overall performance of the process. There are various extraction rate controlling mechanisms mentioned in literature. In this section, different mechanisms which may influence the extraction rates in *SX* processes are highlighted including the mathematical description of these mechanisms.

3.3.1 Mechanism 1: Rate of extraction for a chemically controlled *SX* process

When the rate of a chemical reaction is controlled by the concentration of the reagents, the concentrations in both the bulk solution and at the interface are assumed to be equal. Accordingly, it is possible to represent the rate of extraction as a pseudo-first-order reaction whilst taking into account the concentration of the platinum chlorocomplex at a certain time in both the organic and aqueous phases - see Eq. 3.1 (Jim *et al.*, 1989; Hoh *et al.*, 1989; Komasawa and Otake, 1983):

$$V_{aq}\frac{dC_{aq}^{t}}{dt} = A\left(k_f C_{aq}^{t} - k_r C_{org}^{t}\right) \qquad \textbf{3.1}$$

where dC_{aq}^{t}/dt is the rate of extraction, k_f and k_r represent the forward and reverse reaction rate constants, respectively, while *A* is the contact area between the two phases and *s* refers to interface between the two phases. Furthermore, when the extraction is at equilibrium *(e)*, the disappearance rate of the solute in the aqueous phase will be minimal such that:

$$k_f = k_r \frac{C_{org}^{e}}{C_{aq}^{e}} \qquad \textbf{3.2}$$

Bearing in mind both Eq. 2.8 and Eq. 3.2, the *KD* may be described in a form which incorporates the forward and reverse rate constant for an *SX* process as follows (Jim *et al.*, 1989; Hoh *et al.*, 1989; Komasawa and Otake, 1983):

$$KD = \frac{k_f}{k_r} = \frac{C_{org}^{e}}{C_{aq}^{e}} \qquad \textbf{3.3}$$

In order to describe the *SX* transfer of the metal of interest into the organic phase and while taking into account the forward reaction constant, Eq. 3.1 becomes:

$$V_{aq}\frac{d\left(C_{aq}^{t}\right)}{dt} = k_f A\left(C_{aq}^{t} - \frac{C_{aq}^{e}}{C_{org}^{e}} C_{org}^{t}\right) \qquad \textbf{3.4}$$

In addition, the linearisation of the conservation of mass equation (Eq. 3.4) may be achieved by integrating Eq. 3.4 in order to obtain:

$$\ln\left(\frac{C_{aq}^{t}-C_{aq}^{e}}{C_{aq}^{I}-C_{aq}^{e}}\right)=-k_{f}a(1+\alpha)t \qquad \textbf{3.5}$$

where; 1) k_f represents the forward mass rate transfer constant for the transfer of the high value cation into the organic phase which, in turn, is dependent on the mass transfer regime identified using the value of the E_a for the individual experiments performed; 2) $\alpha = C_{aq}^{e}V_{aq} \big/ C_{org}^{e}V_{org}$ and 3) $a = A/V_{aq}$. The slope of $\ln\left[\left(C_{aq}^{t}-C_{aq}^{e}\right)/\left(C_{aq}^{I}-C_{aq}^{e}\right)\right]$ versus time (*t*), as highlighted in Eq. 3.5, may be used to determine the appropriate forward reaction rate constant *(k_f)* accordingly.

3.3.2 Mechanism 2: Rate of extraction for a reaction controlled by reagent concentration and diffusion parameters

When the extraction is controlled by reagent concentration and diffusive transport, the concentrations in the bulk solution and at the interface are not equal. For this mechanism, the reaction rate constant *(k_f)* highlighted in Eq. 3.5 is equivalent to the apparent reaction rate constant *(k_{app})*, as a result of either the nature or the combination of the mechanism involved.

3.3.3 Mechanism 3: The rate of extraction for a diffusion-controlled *SX* process

During the mixing of the two phases during *SX*, the solute tends to flow from regions of higher concentration to regions of lower solute concentration and there will, ultimately, be an equalisation of concentration over a period of time. Accordingly, the driving force leading to diffusion is the solute concentration gradient between the aqueous and the organic phases (Laider and Meiser, 1982). Fick (1855), thus, established that the rate of diffusion of a solute across a known area, *A*, may be defined by a J , which is dependent on the diffusion coefficient, D, such that the pseudo-first-order reaction expressed by Eq. 3.1 becomes (Nitsch and Plucinski, 1990):

$$J=\frac{V_{aq}}{A}\frac{dC_{aq}}{dt}=D\frac{dC_{aq}}{dx}=\delta_{f}dC_{aq} \qquad \textbf{3.6}$$

In addition, for a process in which the *SX* process is predominantly diffusive, the rate of transfer and/ or reaction rate constant, k_f as described in Eq. 3.1, is equivalent to the δ_f, for which the rate constant describes the diffusive rate of the solute from the aqueous phase to the organic phase while taking into account the film-layer thickness which provides resistance to mass transfer. Eq. 3.6 will be valid only when there is a minimal diffusion of the solute back into the aqueous phase (reverse reaction, i.e. Eq. 2.14) in comparison to the diffusion of the chlorocomplex into the organic phase.

3.3.4 Identification and evaluation of the mass transfer regime

As discussed in section 2.6.1 (chapter 2), the mass transfer mechanism for the transfer of the platinum chlorocomplex using *Cyanex 921* in kerosene may be evaluated by determining the E_a that is, the E_a obtained from experimental $\Delta H°$ values, such that it is possible to identify the kinetic controlling step. In other words, for a diffusive *SX* process, the E_a is normally < 20 kJ/mol while it is > 40 kJ/mol in the case of a chemically controlled process.

3.4 SUMMARY

The mathematical formulations discussed in this chapter which may be used to evaluate mass transfer parameters fall under a pseudo-first-order rate constant in accordance with the assumptions listed. The rate controlling regime and the role of E_a in determining the kinetic mechanism are also discussed. As highlighted in this chapter the flux of the platinum chlorocomplex may be estimated using the appropriate equation.

CHAPTER 4

MATERIALS AND METHODS

4.1 INTRODUCTION

This chapter describes the methodology and experimental procedure used to conduct the research discussed in this thesis. In order to investigate variables such as pH, temperature, initial platinum concentration and the effect of the *Cyanex 921* concentration on the thermodynamic and kinetic parameters of platinum *SX* using *Cyanex 921* in kerosene, the experiments were conducted in a Lewis reactor as per Nitsch and Plucinski (1990). The phases were mixed by means of constant stirring.

4.2 FACTORIAL DESIGN

A factorial design was used to plan a set of experiments which were aimed at realising the objectives of the research. This method allows the simultaneous examination of the effects of multiple independent variables and their degree of interaction. According to Diamond (1981), the effect of more than one variable on a certain response may normally be determined by a series of simple, comparative experiments. For a one-factor-at-a-time procedure, a total of sixteen experiments would be required for a full design in terms of which the effect of four different variables was to be evaluated. However, with a single matrix design experiment, it is possible to include all the variables so as to enable a valid set of experiments to be conducted with a total of eight trials only for a half-design with four variables (see Table 4.1). Accordingly, the experimental design reported in this project may be referred to as a half factorial design of the type 2^4 (2 refer to the number of levels and 4 denotes the number of factors). Each variable has a high level (+) and a low level (-) that may be evaluated in the experiments. From the four different variables identified, and according to the half factorial design, eight experiments were conducted in order to quantify the kinetic and thermodynamic parameters of platinum *SX* using *Cyanex 921* in kerosene.

Table 4.1: Matrix labelling for a 4-variable experiment

Trial	***pH***	***[Cyanex 921]***	***Temperature***	***[Pt]***	***Treatment combinations***
1	-	-	-	-	No combination
2	-	+	-	+	[Cyanex 921]*[platinum]
3	+	+	-	-	pH*[*Cyanex 921*]
4	-	-	+	+	Temperature*[platinum]
5	-	-	+	+	Temperature*[platinum]
6	+	-	+	-	pH*temperature
7	+	-	-	+	pH*[platinum]
8	+	+	+	+	pH*temperature*[Cyanex 921]*[platinum]

From the matrix labelling of the 4 variables varied in the eight trials, it was possible to deduce the actual extraction rate in individual trials for each experiment. The computation of the data originally gauged and the response in each experiment; that is, loading capacity, concentration ratio etc., were estimated in order to obtain an equation with which to predict the response. This, in turn, made it possible to estimate parameters such as the rate constant, equilibrium concentration, *KD* etc., using Eq. 4.1.

$$Y = \beta_0 + \sum_{i=1}^{k} \beta_i X_i^2 + \sum_{i=1}^{k} \beta_{ii} X_i^2 + \sum_{i=1}^{k-1} \sum_{j=2}^{k} \beta_{ij} X_i X_j \qquad \textbf{4.1}$$

where *Y* is the predicted response and β_i, β_j, and β_{ij} are coefficients estimated from regression and representing the linear, quadratic and cross products of x_1, x_2, x_3 …x_n on the response. A statistical program package, *Design Expert 7.5.1* may be used for the regression analysis to estimate the linear coefficients of the multiple regression equation (Rajasimman *et al.,* 2009).

4.3 EXPERIMENTAL SET-UP

The experiments described in Section 4.4 were investigated in a one-litre batch reactor (see Figure 4.1). The reactor itself was made of Perspex and covered by a Perspex lid so as to prevent evaporation. Three evenly spaced baffles to prevent vortex formation at the gas-liquid interface, each with a width *(*B_W*)* of 10 mm, were fitted inside the reactor. The reactor had an internal diameter *(*D_i*)* of 110 mm and a height *(H)* of 150 mm. The contents of the reactor were kept at a constant temperature in a thermostatic water bath, and agitated by a stainless steel stirrer. A Heidolph electric motor was used to drive the impeller assembly at a constant speed

(76.2 rpms). The speed was set using a photo-contact tachometer. A pH meter was used to measure both pH and temperature (Hanna HI 8314). Before taking measurements, the probe was calibrated using pH 1, 4 and 7 buffer solutions. A scale (Mettler HK 60) was used for the weighing of hexachloroplatinic acid ($H_2PtCl_6.6H_2O$). The equipment set-up and reactor dimensions are illustrated in Figures 4.1, 4.2 and 4.3.

4.4 EXPERIMENTAL MATERIALS

After the wet chlorination process, the platinum is in the form of $PtCl_6^{2-}$; therefore, hexachloroplatinic acid ($H_2PtCl_6.6H_2O$) was used as a source of platinum and was supplied by Metal Concentrators (Pty) Ltd, South Africa. The hexachloroplatinic acid was dissolved in hydrochloric acid (1 M). Tri-*n*-octylphosphine oxide (*Cyanex 921*) was selected as the extractant. This extractant, in turn, was made up into 2 and 8% (v/v) solutions (available as *Cyanex 921* from Cytec Industries Inc., Canada and used without further purification) in an aliphatic diluent, that is, kerosene (supplier by Kimix, South Africa and also used without further purification). The kerosene was also made up to 92 and 98% for the experiments to be conducted. Both *Cyanex 921* and kerosene formed the organic phase with a total organic volume of 100 mL. A synthetic stock solution of the platinum chlorocomplex was made by dissolving 2.65 g of hexachloroplatinic acid ($H_2PtCl_6.6H_2O$) in 1000 mL of dilute hydrochloric acid (1 M). The solution was diluted to specification as required for individual experiments. The platinum aqueous phase, which contained the platinum chlorocomplex, was prepared with distilled water in order to achieve platinum concentrations of 25.26 and 56.25 mg/L. The total aqueous volume was 900 mL. Hydrochloric acid (1 M) and sodium hydroxide (5 M) were used to regulate the pH during the experiments. All chemicals used were analytic grade. A set of eight experiments were conducted with different factors such as pH, temperature, initial platinum and extractant concentration. The low level and high level of the artificial conditions were chosen and are presented in Table 4.2. The extraction process was carried out according to the following procedure.

The organic/aqueous volumetric phase ratio (V_{org}/V_{aq}) of 1:9 was used in the batch reactor, while the required pH and temperature were adjusted accordingly and agitated with mechanical stirring. This particular ratio was chosen to ensure the reproducibility of kinetic data which could be accurately measured. The stirrer was a flat-blade impeller with a secondary turbine impeller (see Figure 4.1) which was adjusted to 10 mm below and above the liquid interface. As a result of its small pumping capacity and low axial flow, the flat blade impeller (stirring paddle) was placed in the aqueous phase while the turbine impeller was placed in the organic phase because of its suitability for mixing immiscible liquids. The two-blade impeller was supplied by

Merck Laboratory (Pty) Ltd (South Africa) and was used to maximise the homogeneity of the mixture and to increase the surface area in order to extract more platinum into the organic phase. The impeller speed was kept at 76.2 rpm in both phases, i.e., between the organic and aqueous phase.

A ±10 mL sample was removed from the aqueous phase for analysis at the following time intervals: 0, 300, and 600, 1200, 2400, 5400 and 10 800 seconds (s). A similar volume was removed from the organic phase so as to maintain a constant phase ratio during the experiments. The samples recovered during the experiment were analysed (see section 4.5) for platinum concentration.

Table 4.2: Conditions for the half factorial experimental design

Parameters	***Test 1***	***Test 2***	***Test 3***	***Test 4***	***Test 5***	***Test 6***	***Test 7***	***Test 8***
[*Cyanex 921*] %(v/v)	2	2	8	2	8	2	8	8
pH	1	1	2	2	2	2	1	1
[Pt(IV)] (mg/L)	28.96*b	56.36*b	25.32*a	44.46*b	47.77*b	25.26*a	25.43*a	55.22*b
Temperature (K)	298	318	298	298	318	318	318	298

***Average measured platinum concentration using ICP-ES (t = 0)/a-low level, b-high level*

Overall, the selection of the values of the operating parameters was based on:

- Mhaske and Dhadke (2001a) recommend the extraction of the platinum chlorocomplex at a log *$[H^+]$* range of -1.5 to -1 as it is possible to implement the platinum extraction successfully within this range. However, in this study, the log *$[H^+]$* range used was from -1 to -2 as platinum precipitation had been observed at a pH of 3 (log *$[H^+]$* = -3) during preliminary experiments. Accordingly, this pH range was selected to ensure the success of the *SX* process evaluated;
- the selection of the platinum concentration used in this study was based on both economic reasons and the literature reviewed;
- the *Cyanex 921* concentration used, namely, 2 to 8% (v/v), was selected to ensure the reproducibility of the kinetic data results. The range evaluated was selected based on the use of *Cyanex 921* concentration in platinum studies (see Table 2.3 for more information);
- the selection of the range of temperature from 298 to 318 K was based on research conducted by Mhaske and Dhadke (2001b). In their research, the temperature optimum and range used was from 283 to 333 K. The selected temperature range for this study was 298 to 318 K, which falls within the temperature range determined by Mhaske and Dhadke (2001b).

4.5 ANALYTICAL METHODS

Inductively coupled plasma-emission spectroscopy *(ICP-ES)* (BemLab Pty Ltd, South Africa) was used to determine the concentration of the platinum in the aqueous phase while the platinum in the loaded organic phase was determined by a mass balance of the platinum both before and after extraction.

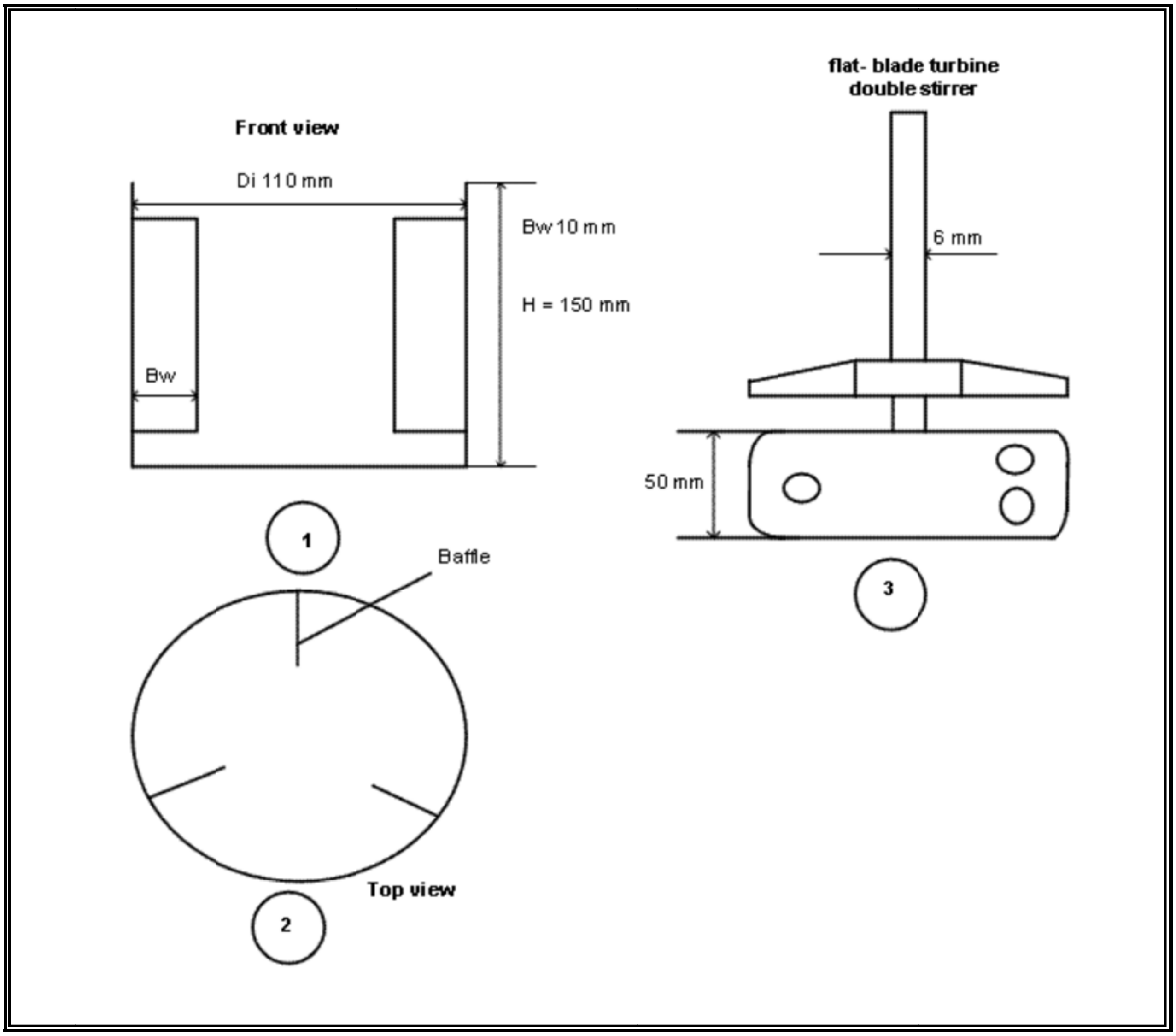

Figure 4.1: Diagram of the experimental apparatus: (1) front view, (2) top view, (3) flat-blade turbine double stirrer

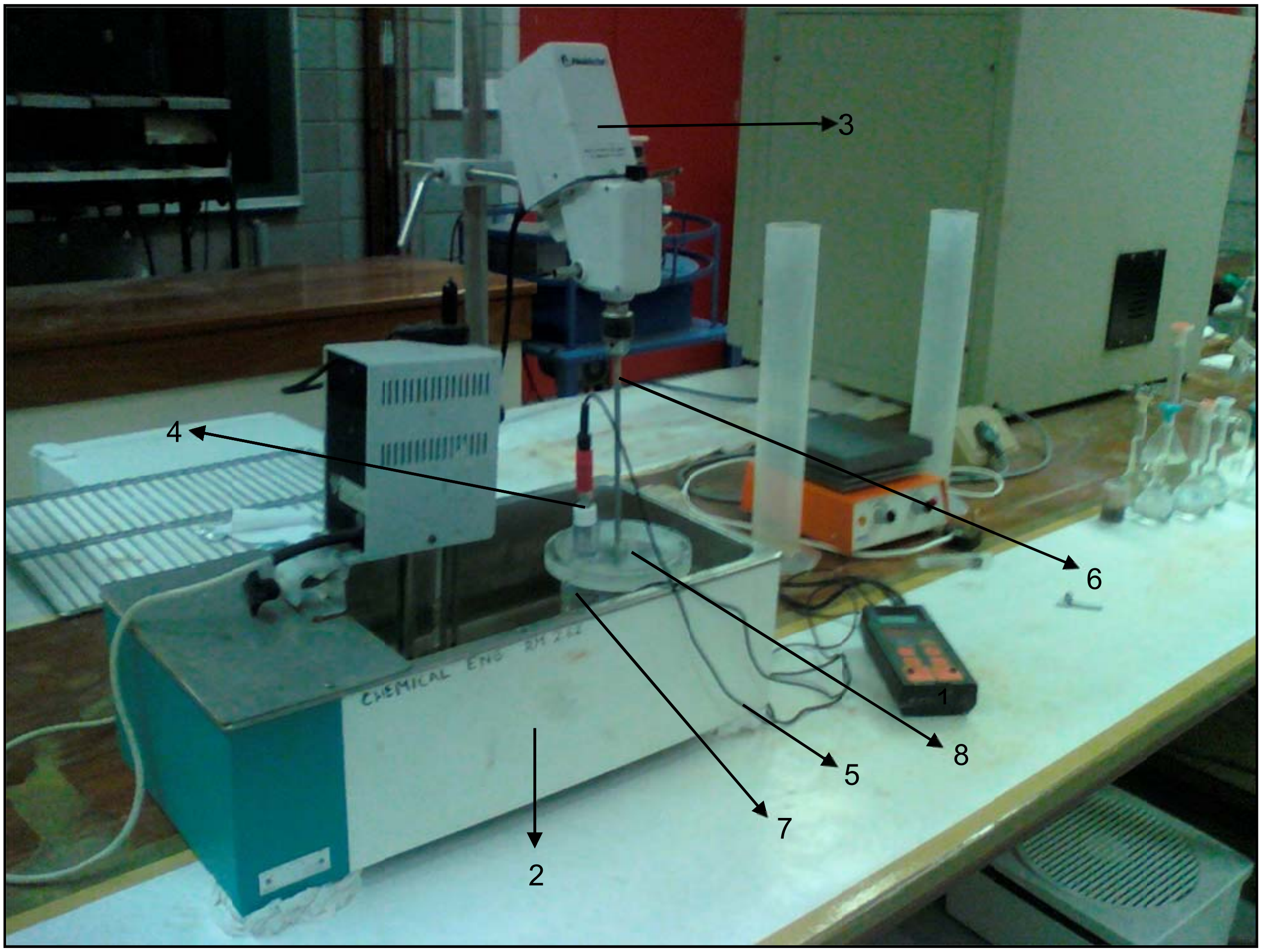

Figure 4.2: ***SX*** **experimental setup: (1) pH meter Hanna HI 8314, (2) water bath, (3) Heidolph variable speed overhead stirrer, (4) Probes Hanna HI 1053B-1 and Hanna Hi 7662-T for pH, (5) temperature measuring, (6) flat blade turbine double stirrer, (7) batch reactor and (8) lid**

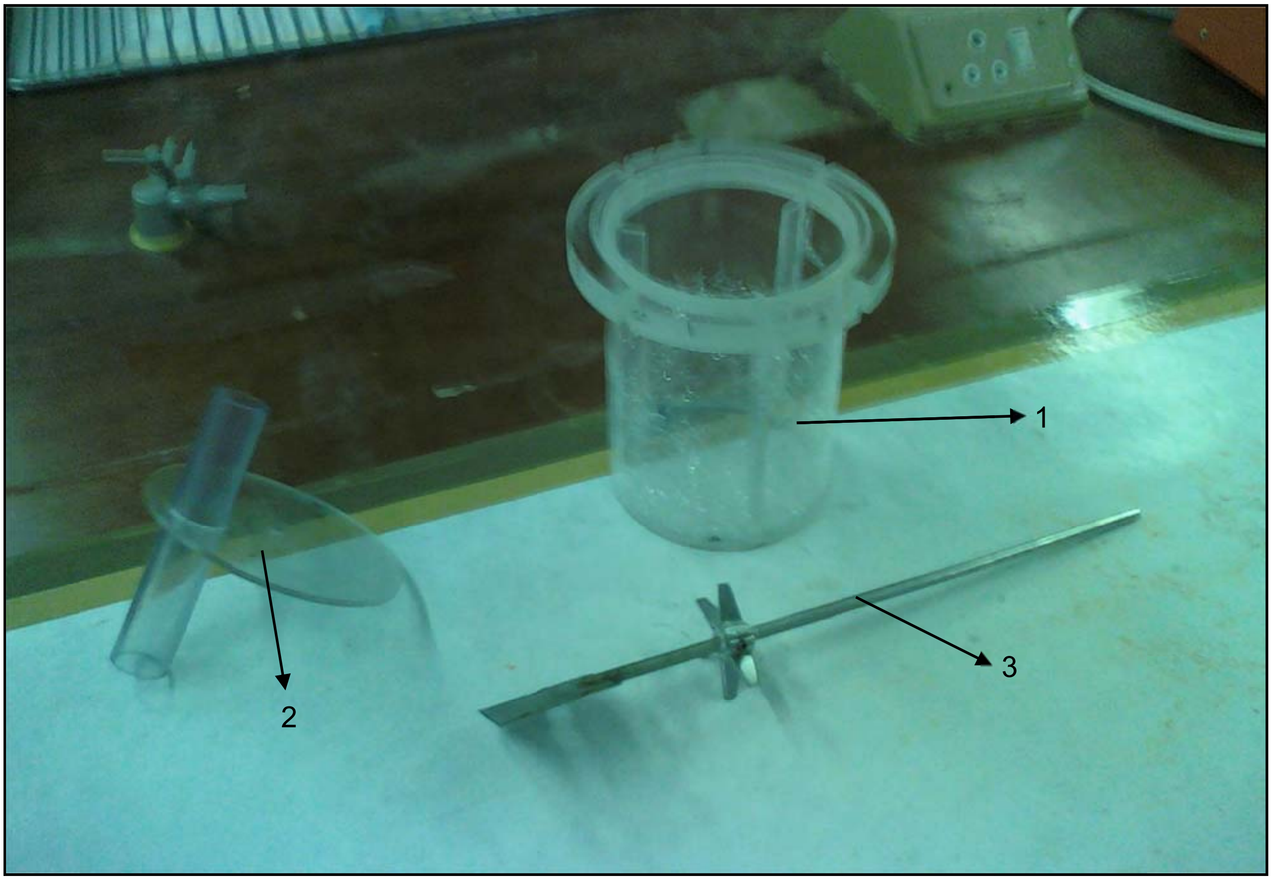

Figure 4.3: Representation of (1) reactor with three evenly spaced baffles, (2) lid, (3) flat blade turbine double stirrer

CHAPTER 5

RESULTS

5.1 INTRODUCTION

This chapter discusses the conditions that influence the performance of a platinum-based *SX* process, the corresponding *KD*, the kinetic rate constant and thermodynamic parameters using *Cyanex 921* in kerosene. The effects of temperature, pH, low *Cyanex 921* concentration and the initial platinum concentration were investigated in order to elucidate their impact on the overall platinum extraction process. The evaluation was performed by varying the test conditions. The results obtained are reported in the subsequent sections.

5.2 EXTRACTION RATIO

The extraction of the platinum chlorocomplex was determined using a half factorial design of the type 2^4. As shown in Figure 5.1 and Appendix B.1, three distinct patterns were identified. Experiments 3, 4, 5 and 6 yielded concentration ratios (C_t/C_i) between 0.85 and 0.89 at equilibrium (*KD* < 1.55); while concentration ratios of 0.65 to 0.68 (*KD* < 4.73*)* and < 0.5 *(KD* > 8.62) were determined for tests 1 to 2 and 7 to 8, respectively. The experiments with concentration ratios < 0.5 were characterised by a high pH (pH = 2) and a low *Cyanex 921* concentration (2% v/v) compared to tests 7 and 8 which had a low pH (pH = 1) and a high *Cyanex 921* concentration. By increasing the *Cyanex 921* concentration, the increase in the exchange sites in the organic phase escalated while the low pH (with an increase in H^+ concentration) influenced the transfer of the platinum chlorocomplex onto the organic phase, as suggested by the mechanism depicted in Eq. 2.14. The influence of the test conditions on the *KD* values (Table 5.1) was such that higher *KD* values > 8.62 were observed for low pH and high *Cyanex 921* concentration, compared to experiments in which a higher pH and low *Cyanex 921* concentration were used. By lowering the *Cyanex 921* concentration from 8 to 2% (v/v), the *KD* values obtained were reduced by > 50%. This indicated that the *SX* process evaluated was dependent on a high *Cyanex 921* concentration and low pH. Overall, it was determined that the concentration ratio (C_t/C_i) was minimally influenced by both the temperature and the increase in the platinum concentration in the aqueous phase at a low pH.

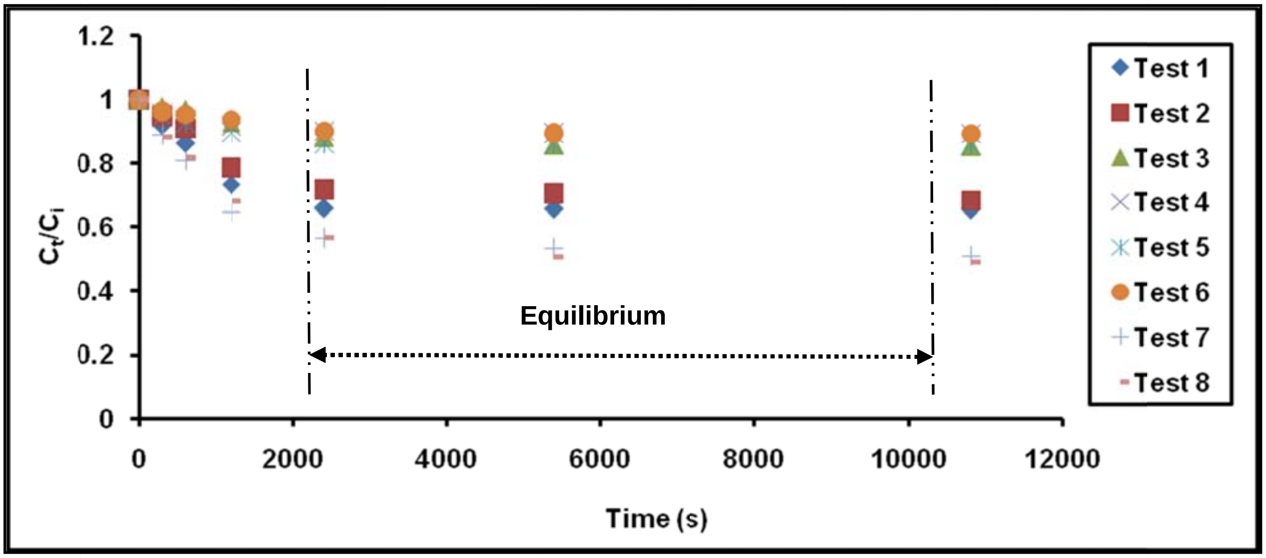

Figure 5.1: The platinum concentration ratio (C_t/C_i) over a period of time (see test conditions presented in Table 4.2)

5.3 LOADING OF THE EXTRACTANT

In order to determine the concentration of the platinum chlorocomplex for loading calculations, that is in the organic phase, a material balance (Eq. 2.8) was used in order to evaluate the disappearance of the platinum chlorocomplex from the aqueous phase. It was assumed that the quantity of the platinum chlorocomplex which disappeared from the aqueous phase was loaded onto the organic phase.

From Figure 5.2 (numerical values are highlighted in Appendix B.2), it was observed that the equilibrium platinum chlorocomplex loading was 253.9 mg/L (determined using Eq. 2.7) for which the transfer of the chlorocomplex onto the organic phase was conducted with an 8% (v/v) *Cyanex 921* concentration, a temperature of 298 K and a pH of 1 (test 8). This phenomenon was attributed to both the high initial platinum concentration and the high *Cyanex 921* concentration (8% v/v) which provided a considerable number of exchange sites for the transfer of the platinum chlorocomplex from the aqueous to the organic phase. The theoretical loading for test 8 was determined as 507.2 mg/L. This loading was assumed to be equivalent to the complete loading of the available platinum chlorocomplex in the aqueous phase, that is, the transfer of 56.36 mg/L, to the organic phase. If the latter is taken into consideration, the equilibrium loading of the platinum chlorocomplex into the organic phase represented ~50% only, achieved within 2400 seconds which, in turn, indicates that the *SX* conditions and the mass transfer used in test 8 were slow.

Similarly, the lowest loading was identified for the following conditions: pH of 2, *Cyanex 921* concentration of 2% (v/v), initial platinum concentration of 25.26 mg/L and a temperature of 318 K. Overall, it was determined that a low pH, high initial platinum chlorocomplex concentration and a high *Cyanex 921* concentration increased the platinum loading onto the organic phase. Furthermore, the results obtained from the experiments showed that loading decreased with an increase in pH, irrespective of temperature and increases in extractant concentration. This indicated that the *SX* process under investigation was highly dependent on low pH.

From the extraction ratio determined, it was expected that tests 7 and 8 would have higher loading in comparison with the other tests conducted. However, for test 7, the loading was determined to be 111.96 mg/L a value which was lower when compared to the results of test 2. In test 7, a lower concentration of the platinum chlorocomplex was used compared to tests 2 and 8. This phenomenon was attributed to the H^+ competition in the *SX* process, that is, for lower concentrations of the platinum chlorocomplex, the H^+ concentration present in the *SX* process dominated active exchange sites on the *Cyanex 921*. A similar phenomenon was observed by Martinez *et al.* (1997) who conducted a study in which a decrease in the extraction of gold (Au) was observed in highly acidic *SX* conditions. Alguacil (2004) also reported this phenomenon for an *Au(III)-HCl-Cyanex 921 SX* process. In order to overcome this behaviour, it is possible to use a higher concentration of the *Cyanex 921* as observed when tests 7 and 1 were compared. Both these tests had a lower initial platinum chlorocomplex concentration while a pH of 1 was maintained. The difference in the higher loading for test 7, when compared to test 1, may be attributed to the fact that an 8% (v/v) of *Cyanex 921* was used in test 7 while a 2% (v/v) concentration was used for test 1.

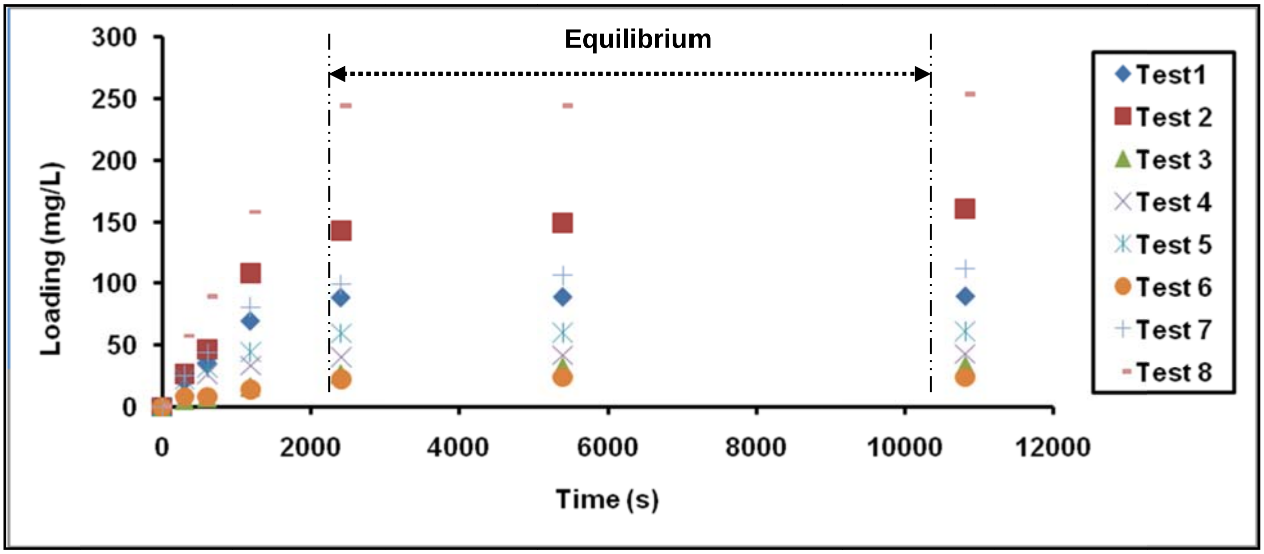

Figure 5.2: Loading of the extractant over a period of time (see test conditions illustrated in Table 4.2)

5.4 DISTRIBUTION RATIO

The *KD* may be defined as a fundamental parameter in terms of the *SX* process. From the results obtained experimentally and presented in Table 5.1, a *KD* of up to 9.40 was achieved. Test 8, in which a high *Cyanex 921* concentration was used, provided the highest *KD*. However, a similar result was not observed in test 7 in which an 8% (v/v) extractant concentration was used. This finding may be attributed to the lower concentration values of platinum used for the experiments. As observed from the equation for the platinum extraction process indicated in chapter 2 (Eq. 2.14) the low pH also assisted in increasing the *KD*. The results obtained in this study showed that the *KD* decreased with an increase in pH (pH = 2), irrespective of temperature and increases in platinum concentration. This would indicate that both a low pH and the high *Cyanex 921* concentration (8% v/v) were the main determining parameters which influenced the *KD*. A similar phenomenon was observed by El-Dessouky *et al.* (2008). In their study an increase in the *KD* of Zn(II), Fe(II), Fe(III) and Cd(II) was observed using a high *Cyanex 921* concentration in an acidic chloride medium *SX* conditions. Furthermore, this behaviour has been observed in other *SX* processes in which a low pH was used.

Table 5.1: Experimental distribution ratio determined using Eq. 2.9

Test	*Experimental KD*
1	4.73
2	4.18
3	1.55
4	1.08
5	1.49
6	1.07
7	8.62
8	9.40

5.4.1 Factorial experimental design

A half factorial design of the type 2^4 was used in order to predict both the response and the influence of the parameters evaluated on individual tests. This was achieved by taking into account experimental results for extraction ratio and loading capacity (Figures 5.1 and 5.2 - see numerical values in Appendices B.1 and B.2) for which linear coefficients were estimated using a statistical *SX* design software *Design Expert 7.5.1* (see Table 5.2).

Table 5.2: A representation of the linear coefficients for a half factorial design experiments

Factors	*Factors*	*Linear coefficients*
		6.81
pH	-	-2.89
Initial platinum concentration	-	0.01
Cyanex 921 concentration	-	1.45
Temperature	-	-0.06
pH	Initial platinum concentration	-0.01
pH	*Cyanex 921* concentration	-0.69
pH	Temperature	-0.03

If *Y* is the response variable which predicts the experimental distribution ratio (*KD)*, then the multiple regression equation (Eq. 4.1 listed in chapter 4 (section 4.2)) with the four parameters under evaluation, while taking into account the linear coefficients in Table 5.2, becomes:

KD = 6.81 - 2.89*[pH] + 1.45*[*Cyanex921*] + 0.01*[initial platinum concentration] - 0.06*[Temperature] - 0.01*[pH]*[initial platinum concentration] + 0.69*[pH]*[*Cyanex 921* concentration] - 0.03* [pH]*[temperature] **5.1**

The mean absolute deviation *(MAD)*, which is a mean of the sum of the overall errors between actual and predicted *KD* values, was calculated. In this case, the *MAD* was equivalent to 0.07 which implies minimal deviation between both actual and predicted *KD*. It was noticed that the highest deviations in the results obtained were for tests 4 and 6. Overall, the deviation was in the range of 0.2 to 0.13. Furthermore, by plotting the actual and the predicted *KD* values (see Table 5.2) against each other, a linear regression analysis provided a correlation coefficient (R^2) value of 0.99. This, in turn, implied a good correlation between the predicted and the experimental *KD* values with a relative error of 1.74% - see graphical illustration in Figure 5.3.

Table 5.3: Representation of the test-predicted *KD* and *MAD*

Test	***Experimental KD***	***Predicted KD***	***Absolute error***
1	4.73	4.64	0.09
2	4.18	4.24	0.06
3	1.55	1.62	0.07
4	1.08	1.18	0.1
5	1.49	1.53	0.04
6	1.07	1.20	0.13
7	8.62	8.65	0.03
8	9.40	9.38	0.02
MAD= (∑ errors of each test)/number of test (8)			0.07
Overall relative error = MAD/average KD			1.74%

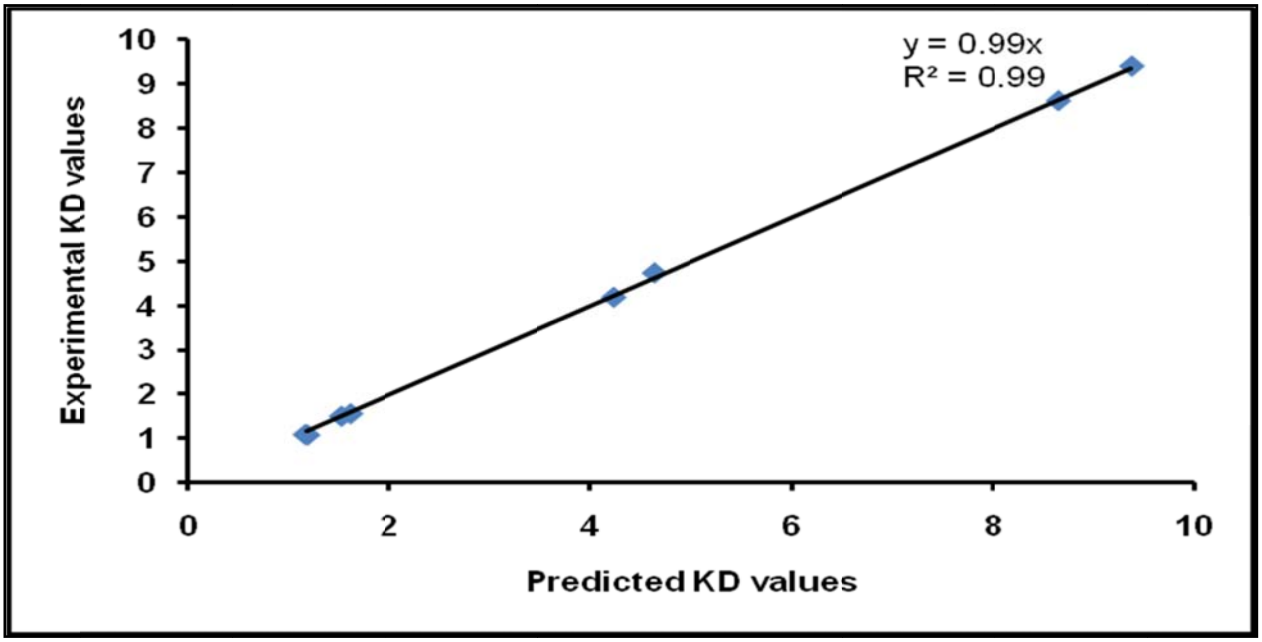

Figure 5.3: A graphical representation of the linear relationship between actual and predicted values of the distribution ratio

5.4.2 Sensitivity analysis

The factorial experimental design model (Eq. 5.1) was developed from the experimental data and represents the effective *KD* for the experimental conditions evaluated. This factorial experimental design model was used to assess the sensitivity of the *SX* process using the following base parameters: reactor temperature of 298 K, *Cyanex 921* concentration of 2% (v/v), pH of 1 and initial platinum concentration of 25.26 mg/L, respectively. The identification and classification of base parameters assisted in the evaluation of the *SX* process researched and facilitated the evaluation of the effectiveness of the extraction conditions used and their applicability. The sensitivity analysis focused on the variation of the base parameters defined from low values (Table 4.2) to high values (reactor temperature of 318 K, *Cyanex 921* concentration of 8% (v/v), pH of 2 and initial platinum concentration of 56.36 mg/L).

5.4.2.1 Effect of pH

The influence of pH was ascertained by determining the platinum *KD* in the pH range studied (1 to 2) - see Figure 5.4 (numerical values listed in Appendix C.1). It was observed that an increase in pH resulted in a decrease in the *KD*. It is possible to offer a tentative explanation of the relative decrease of the *KD* by applying Le Chatelier's principle to the stoichiometry of the platinum *SX* reaction under consideration. The decrease in the *KD* implies that an increase in pH, that is, the reduction of the ionic hydrogen (H^+) concentration in the aqueous phase, resulted in a shift in the proposed reaction (Eq. 2.14, chapter 2) from the right-hand side to the left-hand side, thus causing the observed decrease in the *KD*. An increase in the H^+ concentration in the aqueous phase favoured the extraction of the platinum as compared to tests conducted at a high pH. The resultant plotting of *log KD* versus pH gave a linear equation with a negative slope, thus indicating that, when the pH value was increased to 2, the increase in the concentration of the extractant to 8% (v/v) contributed very little to the extraction of the platinum chlorocomplex.

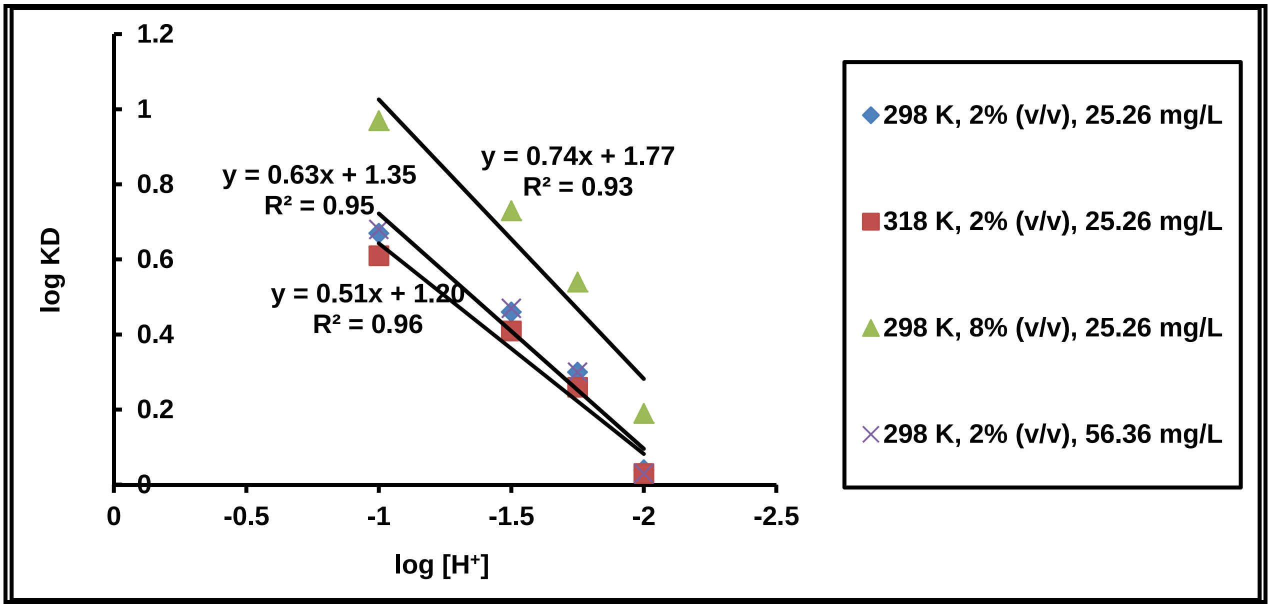

Figure 5.4: A graphical representation of the effect of pH on the platinum *KD*; Legend key: Column 1: temperature, column 2: *Cyanex 921 concentration*, column 3: initial platinum concentration

The increase in temperature from 298 to 318 K in the pH range (1 to 2) under investigation had a negative effect on the *KD*. At a low pH, an increase in temperature reduced the platinum *KD* by 14.19% while, at a high pH, the reduction was 2.73%. The relative decrease in the platinum *KD* may be justified by the fact that an increase in temperature reduces the stability of the platinum chlorocomplex in the organic phase and also by the fact that the extraction of the platinum was not favourable from left to right. Kumar *et al.* (2008) reached a similar conclusion in their research in which a comparison of *SX* studies on platinum in acidic solutions using *Cyanex 302* was conducted. In addition, by increasing the *Cyanex 921* concentration from 2 to 8% (v/v), the variation in pH influenced the platinum *KD* in such a way that, at a low pH, an increase in the *Cyanex 921* concentration to 8% (v/v) enhanced both the extraction and the *KD* by 96.61% while, at a high pH, 40.91% only was achieved. Similarly, an increase in the initial platinum concentration was determined not to influence the effect of pH on the *KD*, that is, the platinum concentration increased in both phases although the *KD* remained constant (see section 5.4.2.4 for more information).

In view of the fact that pH is directly related to the H^+ concentration in any solution, the data, that is, the slope, used in Figure 5.4 may be used to determine the pairing of H^+ moles with *Cyanex 921* such that it is possible to obtain an appropriate mechanism for the stoichiometric reaction. The variation in the slope was dependent on the parameters used in each test which indicated that the involvement of H^+ moles in each case differed. The aim of Table 5.4 was to indicate the number of H^+ moles involved in each stoichiometric reaction for the individual tests. Overall, a high value of the slope was observed for conditions in which the *Cyanex 921* concentration was high, that is 8% (v/v).

Table 5.4: Determination of the number of H^+ moles involved in the *SX* process

Test	***Conditions***	***Number of H^+ moles involved in the stoichiometric reaction***
1	298 K, 2% (v/v), 25.26 mg/L*	≈0.6 [base case conditions]
2	318 K, 2% (v/v), 25.26 mg/L*	≈0.5
3	298 K, 8% (v/v), 25.26 mg/L*	≈0.7
4	298 K, 2% (v/v), 56.36 mg/L*	≈0.6

**Initial Pt chlorocomplex concentration*

5.4.2.2 Effect of *Cyanex 921* concentration

The effect of *Cyanex 921* concentration on the *KD* was evaluated with respect to the base conditions selected. It was observed that the *KD* increased with an increase in the *Cyanex 921* concentration (see Figure 5.5 and numerical values in Appendix C.2). As described by Mhaske and Dadke (2001a) this increase was as a result of an increase in the amount of complexation sites available in the organic phase for which it was possible to attach the platinum chlorocomplex. However, further analysis was necessary in order to reach a thorough understanding of the involvement and the role of the extractant on the *SX* process researched.

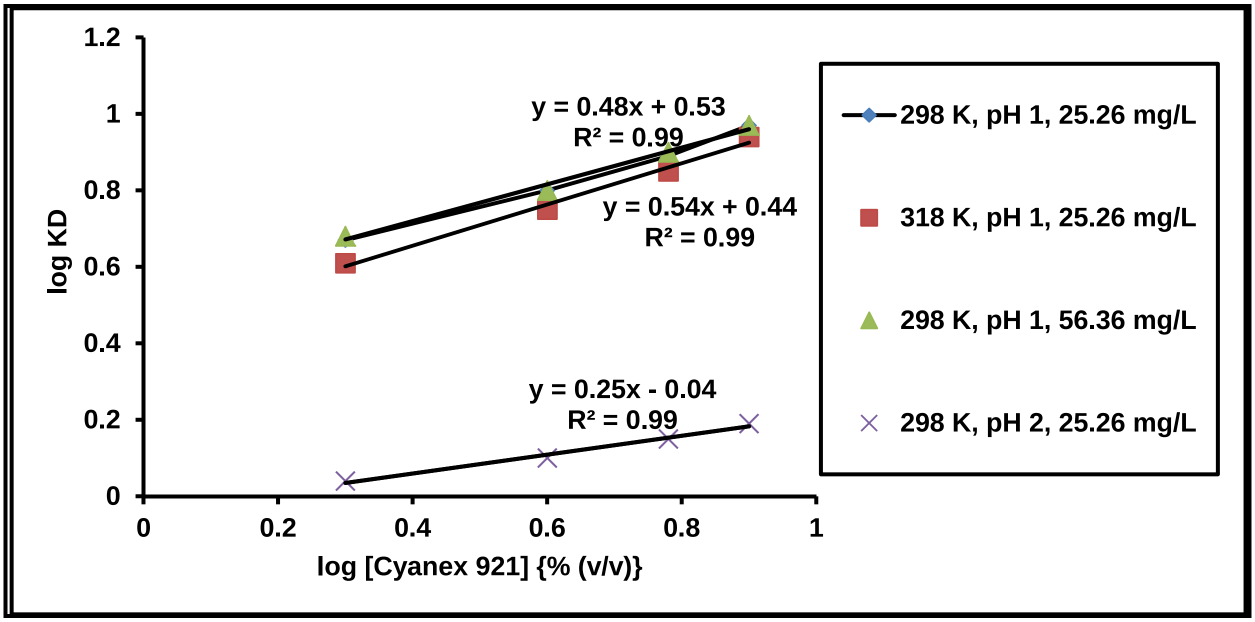

Figure 5.5: A graphical representation of the effect of the *Cyanex 921* concentration on the platinum *KD*; Legend key: column 1: temperature, column 2: pH, column 3: initial platinum concentration

If the *log KD* versus *log [Cyanex 921]* is plotted, the individual tests investigated may provide additional information on the stoichiometric reaction involved. The slope of a graphical representation in terms of which *log KD* versus *log [Cyanex 921]* is presented may provide information on the molar involvement of the extractant in the *SX* process. The slope may be presented mathematically as *m = log KD/log [Cyanex 921]*. In such a case the slope indicates the number of active extractant moles involved in the *SX* process. A similar methodology was used to evaluate the number of extractant moles involved in a solvating extractant (Cyanex 923) used for a titanium (IV)-acidic chloride *SX* process (John *et al.*, 1999). Using the information presented in Figure 5.5, specifically, the slope of individual graphs, Table 5.5 was devised to indicate the number of extractant moles involved in each test.

Table 5.5: Determination of the number of extractant moles involved in the *SX* process for the platinum chlorocomplex under different conditions

Test	*Conditions*	*Extractant moles involved in the stoichiometric reaction*
1	298 K, pH 1, 25.26 mg/L*	0.48 (12/25 ≈ 0.5) [base case conditions]
2	318 K, pH 1, 25.26 mg/L*	0.54 (27/25 ≈ 0.5)
3	298 K, pH 1, 56.36 mg/L*	0.48 (12/25 ≈ 0.5)
4	298 K, pH 2, 25.26 mg/L*	0.25 (1/4)

**Initial platinum chlorocomplex concentration*

In terms of tests 1, 2 and 3, the slope was approximately equivalent to 0.5, which, in turn, indicated that half a mole of the *Cyanex 921* was involved in the transfer of one mole of the platinum chlorocomplex, while a quarter mole of the extractant was involved in test 4. Furthermore, these results confirmed the effectiveness of the *SX* process under low pH conditions; thus suggesting that the stoichiometric reaction (Eq. 2.14) changes, depending on the conditions prevailing in the *SX* process. If the pH is increased to 2 there will be limited extractant moles involved in the *SX* process under consideration. The implications of these findings are as follows; 1) It is essential that the stoichiometric equation be revised when mass transfer computations are evaluated to determine the rate kinetics, and 2) the change in temperature has a minimal influence on the *SX* process while the distribution ratio is independent of the initial platinum concentration.

5.4.2.3 Effect of temperature

Thermal influences on the *KD* for the *SX* process researched were investigated and are presented in Figure 5.6 (see Appendix C.3 for numerical values). The temperature increases investigated were in the range of 298 to 318 K. It was observed that the platinum *KD* decreased insignificantly (~3 to ~9%) for *SX* conditions in terms of which the pH was 1, while a 25% decrease was observed at a pH of 2. Lee *et al.* (2009a,b) and El-Dessouky *et al.* (2008) offer a tentative explanation for the relatively minute decrease in the platinum *KD* for those tests in which the pH was maintained at 1, namely, that an increase in temperature may decrease the stability of the platinum chlorocomplex in the organic phase. Furthermore, it was mentioned by El-Dessouky *et al.* (2008) that the exothermic nature of a *SX* process may also influence the stability of the high-value species in the organic phase. In other words, when a pH of 2 was used, the instability of the platinum chlorocomplex in the organic phase becomes substantial in comparison to conditions in which a pH of 1 was used. This evidence is also supported by the stoichiometric equation in terms of which high pH conditions influence the transfer of the platinum from the organic to the aqueous phase (Eq. 2.14). Overall, this implies that it is possible to implement the *SX* process at an ambient temperature (25°C/298 K) which, in turn, would diminish the energy requirements if the process were to be implemented on a larger scale. Although the diluent used in this study, that is, kerosene, is less flammable than other diluents, for example toluene, etc., operating the *SX* process under an ambient temperature would provide a safer operational environment.

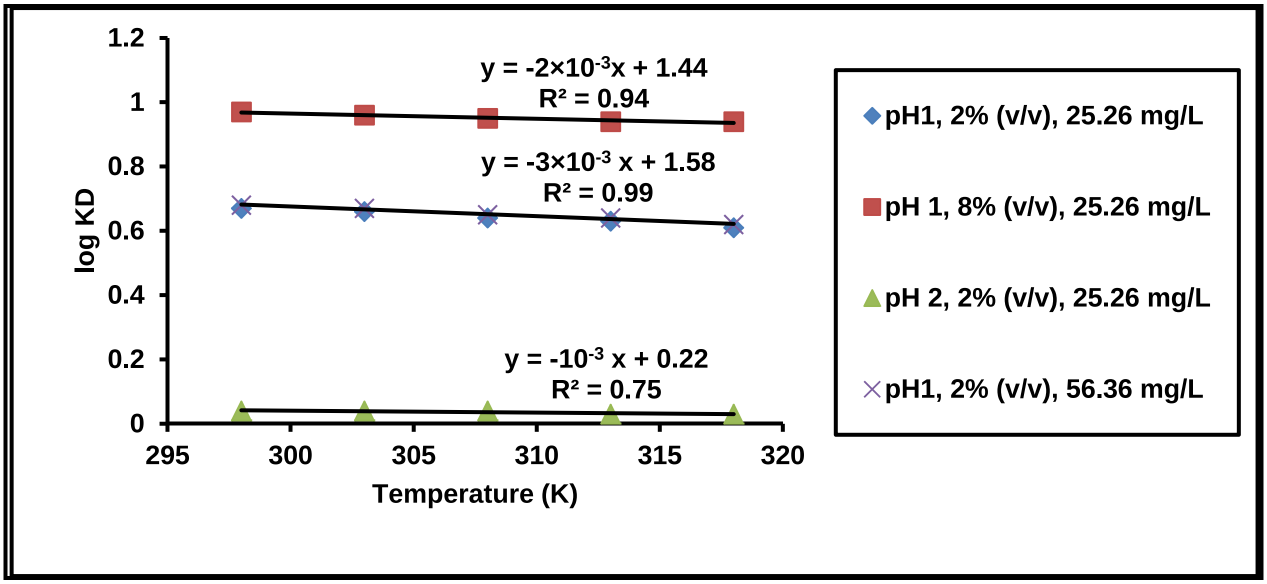

Figure 5.6: A graphical representation of the effect of temperature on the platinum *KD*; Legend key: column 1: pH, column 2: *Cyanex 921* concentration, column 3: initial platinum concentration

5.4.2.4 Effect of initial platinum concentration

As discussed in the above analysis of the effects of temperature, the increase in the initial platinum concentration (varied between 25.26 to 56.36 mg/L) had a negligible effect on the *KD* - see Figure 5.7 (Numerical values listed in Appendix C.4). It was found that the *KD* was independent of an increase in the initial platinum concentration in the aqueous phase, that is, the extraction was not drastically favoured from left to right as suggested by the stoichiometric equation (Eq. 2.14) although, for a high extractant concentration, the actual *KD* was higher in value as compared to the other conditions evaluated. The slope of the plot, *log KD* versus *log [initial Pt concentration],* indicated that the degree of distribution in the two phases was similar under the experimental conditions evaluated.

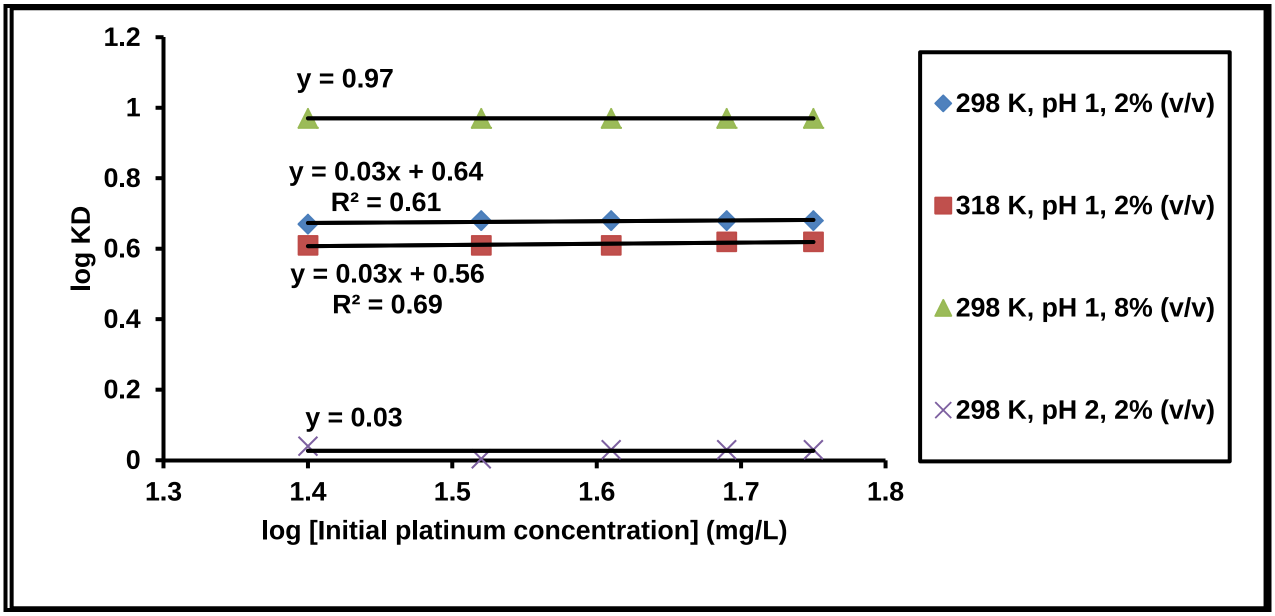

Figure 5.7: A graphical representation of the effect of the initial platinum concentration on the platinum distribution ratio; Legend key: column 1: temperature, column 2: pH, column 3: [*Cyanex 921*]

5.4.2.5 Determination of the nature of the extracted species and favourable extraction conditions

The nature of the extracted species was determined by analysing the experimental data obtained with the conventional slope analysis method (see sections 5.4.2.1 to 5.4.2.4). The nature of the extracted species of platinum (IV) by *Cyanex 921* in kerosene was investigated by varying the initial platinum concentration, *Cyanex 921* concentration and the acidity of the SX process. As previously discussed, 1) the distribution ratio *(KD)* was independent of the initial platinum concentration and 2) the plot of *log KD* versus *log Cyanex 921* suggested that at a high concentration of *Cyanex 921*, the trendline had a slope of ~0.5 which was closer to unity (1). This showed that one ligand reacts with one mole of $PtCl_6^{2-}$ under the following experimental conditions: pH 1, temperature of 298 K and initial platinum concentration of 25.26 or 56.36 mg/L. Furthermore, Figure 5.4 indicated that at a low concentration of H^+ a linear trendline provided a slope 0.74 which was closer to 1, confirming that one mole of H^+ was involved in the stoichiometric reaction under experimental conditions as explained above, i.e., temperature 298 K, *Cyanex 921* of 8% (v/v) and initial platinum concentration of 56.36 mg/L. The probable extracted species is $HPtCl_6^-.TOPO$. Thus, taking into consideration these results, Eq. 2.14 can be rewritten as indicated in Eq. 5.2.

$$\mathrm{PtCl_6^{2-}}_{(aq)} + \mathrm{H^+}_{(aq)} + \mathrm{TOPO}_{(org)} \xleftrightarrow{K_{ex}} \mathrm{HPtCl_6^-.TOPO}_{(org)} \qquad \mathbf{5.2}$$

If $HPtCl_6^-.TOPO$ is assumed to be the only species formed in the organic phase, with the relationship between *KD* and the K_{ex} as (developed from Eq.2.16):

$$\log \mathrm{KD} = \log \mathrm{K_{ex}} - \log[\mathrm{H^+}] - \log[\mathrm{TOPO}] \qquad \mathbf{5.3}$$

5.5 EVALUATION OF THERMODYNAMIC AND KINETIC PARAMETERS

5.5.1 Thermodynamic characteristics of platinum *SX* using Cyanex *921* in kerosene

In thermodynamics, the magnitude of the Gibb's free energy change, $\Delta G°$ forms the fundamental criterion in respect of reaction spontaneity. A reaction occurs spontaneously at a given temperature if the value of $\Delta G°$ is negative and, thus, the extraction of the platinum chlorocomplex using *Cyanex 921* in kerosene researched in this thesis indicated that the extraction occurred spontaneously in all the cases investigated.

The tests were carried out in a temperature range of 298 to 318 K with a variation of the platinum concentration, that is, 25.26 to 56.36 mg/L. The ΔG° values determined using equilibrium *KD* values, ΔG° were found to vary in the range of -5.70 to -0.18 kJ/mol (calculated using Eq. 2.19) which, in turn, indicated the feasibility of both the process and its spontaneous nature. As indicated in the literature reviewed, when the ΔG° is characterised by a large negative number (>> -10 kJ/mol), then the reaction is spontaneous (left to right see Eq. 5.1). Despite the fact that the ΔG° values obtained in this study were of a magnitude which suggested reaction spontaneity, they were, however, not significantly large to indicate the irreversibility of the reaction. This would suggest that the recovery of the platinum chlorocomplex from the organic phase should be easier. According to Ebbing (1993), when ΔG° has a small negative value, there is a significant amount of both products and reactants in solution. In terms of the *SX* process under investigation this meant that there was a significant distribution of the platinum chlorocomplex in both the aqueous and the organic phases.

The values of ΔH° and ΔS° for each experiment were calculated from both the slope and the intercept obtained (see Eq. 2.18 in chapter 2) from a linear regression of the plotting of *log KD* versus *1000/T* - see Figure 5.8 (Numerical values in Appendix D.1.2). The *KD* values used in the analysis conducted in each test were determined using the linear regression model developed in Chapter 4 and represented in Eq. 2.9. It was noticed that the ΔH° values obtained varied in the range of -5.92 to -0.85 kJ/mol for the process under investigation. Despite the fact that this indicated exothermicity, the process does not release excessive energy, thus indicating the suitability of the *SX* process under evaluation for industrial application. For experiments in which the pH value was 2, the ΔH° values were < -1.20 kJ/mol while those conducted at a pH of 1 had ΔH° values > -2.90 kJ/mol. This implies that an increase in temperature may severely reduce the reliability of those *SX* processes in which a pH of 1 was used when compared to tests in which a pH 2 was used (see Figure 5.4 for additional evidence). However, there was a variation in the ΔS° values obtained, that is, two distinct patterns were identified; 1) tests 1, 2, 4 and 6 were determined to have negative ΔS° values (-6.92 to -3.20 J/mol.K) while tests 3, 5, 7, and 8 results indicated that the relevant ΔS° was positive (0.61 to 9.02 J/mol.K).

In general chemistry terms the following is an accepted fact, namely, when a process has a positive ΔS° value while the ΔH° is negative, the process may be classified as strictly spontaneous across a wide range of temperatures. However, for a process with both negative ΔS° and ΔH° values, the process is spontaneous at low temperatures (Ebbing, 1993). This implies that, for tests under similar conditions which yield positive ΔS° values while the ΔH° is negative, the *SX* efficiency may be improved by reducing the temperature. In terms of tests 1 and 2, the low temperature used in test 1 had a positive effect on the experimental *KD* value obtained as compared to test 2 in which the initial platinum chlorocomplex concentration and temperature were increased. The resultant improvement in the *KD* values (test 1 vs. test 2) was in the region of ~13% (pH 1 conditions) while the change in *KD* values for tests 4 and 6 was negligible (pH 2 conditions). Furthermore, in respect of *SX* processes with a positive ΔS°, the ΔH° value for these processes should be a high negative value with the result that the heat generated will favourably enhance the stoichiometric mechanism of such processes. This effect was observed in tests 1 and 2 for which the ΔS° was determined to be a high negative value, i.e., -6.92 and -6.24 J/mol.K respectively, as compared to all the tests evaluated. On the other hand, in tests 4 and 6 in respect of which the ΔH° values were determined as -3.46 and -3.20 kJ/mol, lower *KD* values were observed. Overall, the thermodynamic parameters obtained confirmed the findings of Wenwei *et al.* (2007) who used a Hf-HCl-*Cyanex 921* matrix in their research. It was imperative to determine the thermodynamic parameters representative of experiment conducted for the extraction process, by plotting *log KD* against *1000/T* (see Figure 5.8).

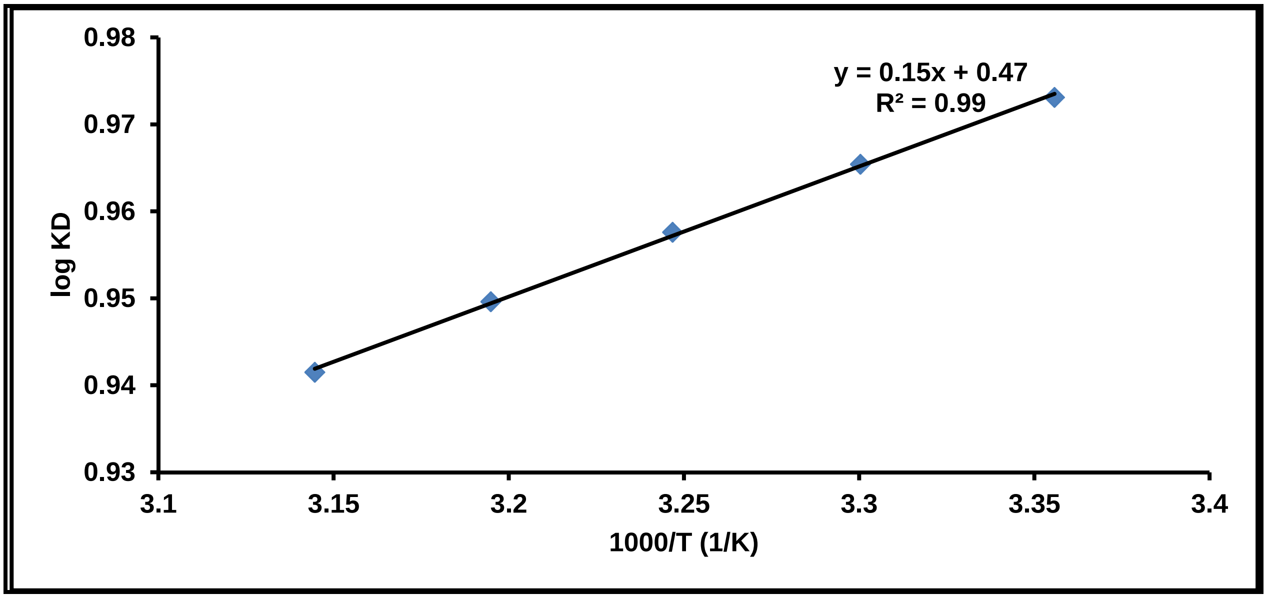

Figure 5.8: A graphical determination of ΔH° and ΔS° (pH 1, [Cyanex 921] 0.18 mg/L and Pt(IV) 55.22 mg/L)

Overall, under the following conditions, pH of 1, *Cyanex 921* of 8% (v/v), initial platinum concentration of 55.22 mg/L, the plot of *log KD* against *1000/T* provided a linear trendline with a positive slope and intercept, indicating the exothermic nature of the extraction process. From the slope, the ΔH° evaluated was -2.87 kJ/mol while the ΔG° was determined to be -5.55 kJ/mol (calculated using Eq. 2.19). This reflected the spontaneity of the extraction process and the ΔS° (9.02) J/mol.K), indicated the affinity of the platinum (IV) towards *Cyanex 921*.

5.5.1.1 Determination of activation energy

An important aspect of the analysis of the kinetic parameters of a chemical reaction is the determination of the E_a. This E_a may be defined as the indispensable energy which is required to initiate a spontaneous chemical reaction such that the reaction will proceed without the need for additional energy. In terms of *SX* processes, the E_a was described as the smallest possible quantity of energy needed for the binding of the high value metal to the organic phase (Murry and Fay, 1995). As indicated in section 3.4 (chapter 3), E_a may be used to determine either the mass transfer regime or the mechanism for the transfer of the platinum chlorocomplex using *Cyanex 921*.

In this study, activated complex theory was employed in order to obtain a thermodynamically consistent formulation of the E_a that was in agreement with the experimental data as described by Moore (1983). This was achieved by taking into account the thermodynamic parameters (see

Appendix D.1.2 for numerical values) calculated in such a way that it became possible to consider a quantitative approach (highlighted in Eq. 2.22) for the determination of the E_a.

The E_a calculated at each test with different parameters varied within the range of -3.44 to 1.76 kJ/mol (determined using Eq. 2.23) over the temperature range studied, that is, 298 to 318 K, which, in turn, indicated that a diffusion-controlled mechanism occurred when the platinum chlorocomplex was transferred from the aqueous bulk phase through the interface into the organic phase. In terms of a diffusion *SX* process, the transfer of the high value metal of interest will be influenced by the rigorous agitation employed in such a process with the result that the rate-limiting transfer parameters will be minimised. In addition, in terms of *SX* processes, a negative E_a would suggest that an increase in the temperature would decrease the overall transfer of the platinum chlorocomplex from the aqueous phase into the organic phase. Indeed, this was the pattern indicated in tests in which a low pH (pH = 1) was used (tests 1, 2, 7, and 8) and for which the E_a was determined to be in range -3.44 to -0.26 kJ/mol. However, this was not the case for tests with a high pH (pH = 2), that is tests 3, 4, 5 and 6 for which the E_a was determined to be 1.26 to 1.78 kJ/mol. Furthermore, under the following conditions, pH of 1, *Cyanex 921* of 8% (v/v) and initial platinum concentration of 55.22 mg/L, the E_a value determined was -0.39 kJ/mol which was within the same order of magnitude as those determined in test 1 to 7.

5.5.2 Extraction kinetics

It may be observed from Figure 5.9 (see Appendix D.2 for numerical values) that a *J* of up to 2.47×10^{-7} mg/mm^2.s was achieved with test 8 yielding the highest *J* as compared to the other tests. This further confirmed the results presented in section 5.3 (loading of the extractant) in terms of which the highest loading achieved was 253.9 mg/L. The increase in loading was attributed to both the high *Cyanex 921* concentration used and the high initial platinum concentration. As observed from the stoichiometric reaction equation for the platinum extraction process under investigation the low pH also assisted in increasing the *J*. In addition, the platinum chlorocomplex *J* decreased with an increase in pH to 2.

For those tests with a pH of 2, that is tests 4 and 5, the higher temperature (318 K) and initial platinum concentration (44.46 and 47.77 mg/L, respectively) had a positive influence on the flux to the effect that a nominal increase was observed as compared to tests 3 and 6. In addition, for test 3, a higher flux of the platinum chlorocomplex was observed as compared to test 6. The difference in this latter case was attributed to the high *Cyanex 921* concentration used in the experiment. Additionally, when the *SX* conditions were, pH of 1, *Cyanex 921* concentration of 8% (v/v) (0.18 mol/L), initial platinum concentration of 55.22 mg/L and temperature of 298 K, the *J* was found to be 4.94×10^{-7} mg/mm^2.s.

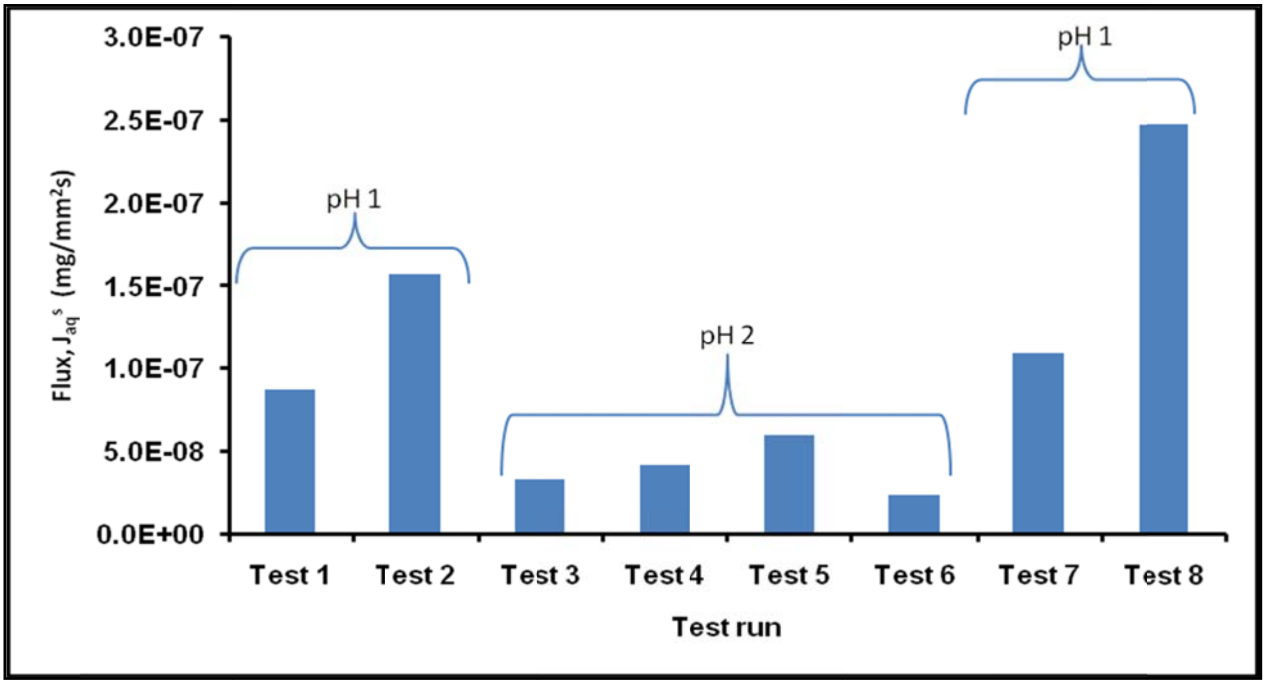

Figure 5.9: A representation of the diffusive flux of the platinum chlorocomplex from the aqueous to the organic phase (see Appendix D.2 for numerical values)

There is limited information on the *J* of a *Pt(IV)-HCl-Cyanex 921* matrix in a *SX* process available to corroborate the flux values obtained in this study. In fact, in order to verify the flux values obtained, it was deemed imperative to evaluate the rate parameters, e.g., the forward diffusive rate constant, that is, mass transfer rate coefficient, for each test and compare the values ascertained with the results published in literature.

In terms of the *Pt(IV)-HCl-Cyanex 921 SX* extraction system under investigation, diffusion was found to be the controlling step during the transfer of the platinum chlorocomplex onto the organic phase (see section 5.5.1.1). The process of the platinum chlorocomplex transfer between two immiscible liquids may be described in terms of Eq. 3.6 (see chapter 3). Indeed, for a diffusion process, the rate constant (k_f) will be equivalent to the δ_f when Eq. 3.6 is used. The mass transfer rate constant presented in this thesis takes into account the film-layer thickness. In this study, the *J* values presented in Figure 5.9 were used to quantify the value of the δ_f, which was, in turn, found to be consistent at 8.77×10^{-3} mm/s across tests 1 to 8 because the stirring speed was maintained at 76.2 rpm for the tests in question. The δ_f as presented in this section may be understood to represent the overall mass transfer coefficient for the *SX* process evaluated. In view of the fact that there is limited information on the diffusion and δ_f for a *Pt(IV)*-HCl-*Cyanex 921* batch-type *SX* process, the rate transfer constant obtained in this study was compared to that obtained for a supported liquid membrane *(SLM)* Au(III)-HCl-*Cyanex 921* process. Despite the fact that the process dynamics of the two designs are different, the δ_f achieved for both processes was in the region of 10^{-3} mm/s, with the *SLM* design achieving a higher rate than the batch-type process used. As the SLM is a pressure-driven process, it may be expected that the δ_f would be higher in comparison to the batch *SX* process under investigation as the latter was operated under ambient pressure conditions. The basis of comparison was the fact that a HCl-*Cyanex 921* matrix was used for both processes.

5.6 SUMMARY

The experiments carried out facilitated an investigation into the influence of the operational parameters on the *SX* process evaluated. It was observed that each of the parameters investigated influenced the extraction of platinum in a different way. The highest loading and theoretical loading possible was as high as 253.9 mg/L and 507.2 mg/L, respectively. These values were obtained under the following conditions: pH of 1, temperature of 298 K, *Cyanex 921* concentration of 8% (v/v) and initial platinum concentration of 55.22 mg/L. The quantitative effect of each parameter on the *SX* process evaluated was evaluated and the analysis response determined using Eq. 5.1, using linear coefficients values obtained from the statistical *Design Expert* software 7.5.1. The stoichiometric of the extracted species was determined by analysing the experimental data using the conventional slope analysis method. The extracted species was found to be $HPtCl_6^-.TOPO$ at a pH of 1 while poor extraction was observed at pH 2. Taking into consideration results obtained from the analysis of the results obtained favorable conditions were: pH of 1, Cyanex concentration of 8% (v/v), temperature of 298 K and initial platinum concentration of 55.22 mg/L.

The thermodynamic parameters, namely, $\Delta H°$, $\Delta S°$ and $\Delta G°$ of the platinum *SX* process using *Cyanex 921,* indicated that the negative value of the $\Delta H°$, confirms the exothermic nature of the platinum extraction process while the positive $\Delta S°$ reflects the affinity of the extractant towards platinum. In addition, the negative value of $\Delta G°$, indicated both the feasibility of the process and its spontaneous nature, conditions which are favourable for complexation. The values of the E_a calculated indicated a diffusion-controlled mechanism that had taken place either in the bulk or near to the interface.

The *J* of the chlorocomplex was found to be 2.36×10^{-8} to 2.47×10^{-7} mg/mm^{2}s which suggests that both the high *Cyanex 921* concentration used as well as the high initial platinum concentration had a positive influence on the process under investigation. On the other hand, the low pH assisted in increasing *J* in such a way that the δ_f was 8.77×10^{-3} mm/s with a stirring speed of 76.5 rpm.

CHAPTER 6

CONCLUSIONS AND RECOMMENDATIONS

6.1 CONCLUSIONS

This study investigated the effect of various parameters, namely, temperature, pH, *Cyanex 921* concentration and initial platinum concentration, on the *KD*. The study was conducted in a laboratory using a bench-scale batch reactor unit with *Cyanex 921* in kerosene and 1 M hydrochloric acid solution. The following conclusions were reached.

The favourable conditions under which the platinum extraction and the loading of the extractant as determined from the batch kinetic results included: 298 K, *Cyanex 921* concentration of 8% (v/v), initial platinum concentration of 55.22 mg/L and pH of 1. Under these conditions the batch test provided a maximum loading with an extraction ratio of ~0.49. The highest loading of the platinum chlorocomplex into the organic phase represented ~50% only within 2400 s which implies that less than optimum *SX* conditions were used.

The use of a factorial experimental design enabled the realisation of a correlation coefficient *(R^2)* of 0.99 when the experimental *KD* and the modelled *KD* were compared. This would suggest that the regression equation used to compare the modelled data generated was, indeed, suitable for the prediction of the values for the *KD* with a mean absolute deviation of 0.07 with a relative error of 1.74%. In terms of the sensitivity analysis, the *SX* process used in this study was significantly influenced by the pH and the concentration of the *Cyanex 921* concentration rather than the initial platinum concentration and temperature. This, in turn, would suggest that different stoichiometric mechanisms are involved with different conditions in the *SX*. The overall results indicated the following: the platinum *KD* decreased insignificantly (~3 to ~9%) with an increase in temperature for *SX* conditions in which the pH was 1, while a decrease of *KD* in the range of 25% was observed at a pH of 2. This, in turn, implies that it is possible to implement the *SX* process at an ambient temperature (25°C/298 K) and this would lessen the energy requirements should the process be implemented on a larger scale.

The thermodynamic parameters, $\Delta H°$, $\Delta S°$ and $\Delta G°$, varied for the individual tests and this further suggested that a variation in the parameters used may have either a negative or a positive effect on a *SX process*. The variation in thermodynamic parameters, in turn, would require the optimisation of the *SX* process in such a way that it would be possible to attain optimal operating conditions. Furthermore, the $\Delta H°$ values obtained confirmed that the process does not release excessive energy which would indicate the suitability of the process in respect of industrial application. On the other hand, the positive entropy reflected the suitability of the extractant for the process evaluated. Overall, the negative $\Delta G°$ values indicated solvation spontaneity with a significant distribution of the platinum chlorocomplex in both the aqueous and the organic phases. In addition, from the $\Delta H°$, $\Delta S°$ and $\Delta G°$, the E_a over the temperature range studied was found to be less than 20 kJ/mol suggesting that all the experiments performed in this study were controlled by a diffusive step. This, in turn, suggests that an increase in the stirring speed might have had a positive influence on the process.

6.2 RECOMMENDATIONS FOR FUTURE STUDIES

The research project reported the kinetic and thermodynamic parameters of platinum *SX* by *Cyanex 921* in kerosene. However, the following aspects were not covered in this thesis and, if the platinum *SX* is to be further improved, these aspects merit investigation:

- optimisation of parameters such as the extractant concentration and pH as these parameters were determined to be influential for the *SX* evaluated;
- specifically in terms of pH, ascertain the effectiveness of a pH lower than 1. This has, in fact, been illustrated in various *metal-HCl-Cyanex 921* matrix research studies;
- determining whether an increase in the stirring speed may positively minimise mass transfer limitations in such a way that the transfer of the platinum chlorocomplex onto the organic phase may be enhanced;
- evaluating the effect of other extractants with an improved capacity to extract the platinum under highly acidic conditions.

BIBLIOGRAPHY

Alguacil, F.J. 2004. Carrier-mediated gold transport in the system *Cyanex 921*-HCl-Au (III). *Hydrometallurgy*, 71(3-4):363-369.

Barnes, J.E. and Edwards, J.D. 1981. Solvent extraction at Acton Precious metal refinery. *Chemistry and Industry*, London, 151.

Baruah, B.P. and Khare, P. 2007. Desulfisation of oxidised Indian coals with solvent extraction and alkali treatment. *Energy and Fuels*, 21:2156-2164

Bernadis, F.L, Grant, R.A and Sherrington, D.C. 2005. A review of methods of separation of the *Pt*-group metals through their chlorocomplexes. *Reactive and Functional Polymers*, 65(3):205-217.

Blumberg, R. 1988. *Liquid-liquid extraction*. New York: Academic Press, 2-6.

Brooks, C.S. 1991. *Metal recovery from industrial wastes*. Chelsea, Michigan: Lewis.

Chavan, M.B., Anuse, M.A. and Lokhande, T.N. 1998. Extraction and separation studies of *Pt* (IV) with *N*-n-octylaniline, *Talanta*, 47(4):823-832.

Cox, M. 1988. Industrial application of solvent extraction*. In developments in solvent extraction*, edited by S. Alegret. Chichester UK: Ellis Horwood, 151.

Cox, M. 1992. Solvent extraction in hydrometallurgy. *In principles and practices of solvent extraction*. Edited by Choppin, R.G; Cox, M; Musikas, C; Rydberg, J New York: Marcel Dekker, 357-412.

Cox, M. 2004. Introduction to solvent extraction*. In solvent extraction: Principles and practice in hydrometallurgy*. Edited: Choppin, R.G; Cox, M; Musikas, C; Rydberg, J, second edition, UK: CRC, 11.

Diamond, W.J. 1981. *Experimental design for engineers and scientists*. New York: Van Nostrands Reinhold Co, 1-117.

Duche, S.N. and Dhadke P.M. 2001. Comparative study of the determination of platinum by extraction with Cyanex 923 and Cyanex 471X from bromide media. *Journal of Chemical Technology and Biotechnology*, 76:1227-1234.

Dziwinski, E. and Szymanowski, J.. 1998. Composition of Cyanex 923, Cyanex 925, *Cyanex 921* and TOPO, *Solvent Extraction and Ion Exchange,* 16(6):1515-1525.

Ebbing, D.D. 1993. *General Chemistry*. Fourth edition. Houghton Mifflin Company.

El-Dessouky, S.I., El-Nadi, Y.A., Ahmed, I.M., Saad, E.A. and Daouad, J.A. 2008. Solvent Extraction Separation of Zn(II), Fe(II), Fe(III) and Cd(II) using tributylphosphate and *Cyanex 921* in kerosene from chloride medium, *Chemical Engineering and Processing: Process Intensification,* 47:177-183.

Grant, R.A.1990. Proceedings of IPMI seminar. *In precious metals recovery and refining*, Allentown, USA: 7.

Gupta, K., Gupta, C.K., Mukherjee, T.K. and Pashev, I. 1990. *Hydrometallurgy in extraction process, volume II.* India: CRC Press.

Harris, B.G., Monette, S., Barry, J.P. and Stanley, R. 1991. *Recovery of pure Pt and Pd*. Toronto, Canada: Noranda Inc.

Hoh, Y, Ju, S. and Chiu, T. 1989. Effect of internal recycle on mixer-settler performance, *Hydrometallurgy*, 23(1):105-518.

Jafarifar, D., Daryanavard, M.R. and Sheibani, S. 2005. Ultra fast microwave assisted leaching for recovery of platinum from spent catalyst, *Hydrometallurgy*, 78(3-4):166-171.

Jim, M., Michel, F.C.and Nobel, R.R. 1989, Kinetics of copper extraction using anti-2-hydroxy-5-nonylbenzophenone oxime. *Industrial and Engineering Chemistry Research*, 28(2): 193-98.

John, S.K., Saji, J., Reddy, M.L.P., Ramamohan, T.R. and Rao, T.P. 1999. Solvent extraction of titanium (IV) from acidic chloride solutions by Cyanex 923. *Hydrometallurgy,* 51: 9-18

Komasawa, I. and Otake, T. 1983. Kinetic studies of the extraction of divalent metals from nitrate media with bis (2-ethylhexyl) phosphoric acid. *Industrial and Engineering Chemistry Fundamentals*, 22: 367-371.

Kumar, J.R., Lee, J.Y., Kim, J.S. and Sohn, J.S. 2008. Comparison of liquid-liquid extraction studies on platinum (IV) from acidic solutions using bis (2, 4, 4-trimethylpentyl) monothiophosphonic acid. S*eparation and Purification Technology*, 63:184-190.

Laider, J.K. and Meiser, H.J. 1982. *Physical chemistry*. Menlo Park, California.: Benjamin/Cummings

Lee, Y.J., Kumar, R.J., Kim, S.J., Park, K.H. and Yoon, S.H. 2009a. Liquid-liquid extraction/separation of platinum (IV) and rhodium (III) from acidic chloride solutions using tri-iso-octylamine. *Journal of Hazardous Materials*, 168:424-429.

Lee, Y.J., Kumar, R.J., Kim, S.J. and Yoon, S.H. 2009b. Extraction and separation of platinum (IV) from acidic chloride solutions using Aliquat 336. *Journal of Industrial and Engineering Chemistry*, 15(3):359-367.

Levenspiel, O. 1999. *Chemical reaction engineering*. Third edition. Canada: John Wiley and Sons, 20-27.

Lo, T.C., Baird, M.H.I. and Hanson, C. 1983. *Handbook of Solvent Extraction*. New York: Wiley, 535-700.

Martinez, S., Sastre, A. and Aguacil, F.J. 1997. Gold extraction equilibrium in the system Cyanex 921-HCl-Au(III), *Hydrometallurgy,* 46(1-2): 205-214.

Mhaske, A.A. and Dhadke, P.M. 2001a. Solvent extraction equilibria for Pt(IV)-HCl-Cyanex 921 and Pt(IV)-HCl-Cyanex 925 systems in toluene. *Chemical Engineering,* 34(1):1052-1055.

Mhaske, A.A. and Dhadke, P.M. 2001b. Extraction separation studies of Rh, Pt and Pd using Cyanex 921 in toluene a possible application to recovery from spent catalyst. *Hydrometallurgy,* 61(2): 143-150.

Mhaske, A. and Dhadke, P. 2002. Extraction separation studies of Os, Ru and Ir using Cyanex 921 in toluene. *Hydrometallurgy,* 63(2): 207-214.

Mishra, S. and Devi, N. 2011. Extraction of copper(II) from hydrochloric acid solution by Cyanex 921. *Hydrometallurgy,* 107: 29-33.

Mohapatra, D., Hong-In, K., Nam, C.W. and Park, K.H, 2007. Liquid-liquid extraction of aluminium (III) from mixed sulphate solutions using sodium salts of Cyanex 272 and D2EHPA. Separation and Purification Technology, 56: 311-318.

Moore, W.J.1962. *Physical Chemistry.* Fourth edition. Great Britain: Prntice-Hall.

Moore, W.J. 1983. *Basic Physical Chemistry*. United States of America: Prentice-Hall.

Morrison, G.H. and Freiser, H. 1957. *Solvent extraction in analytical chemistry*. New York: Wiley.

Murry, J.Mc. and Fay, R.C. 1995. *Chemistry.* Englewood Cliffs, NJ: Prentice-Hall.

Nitsch, P. and Plucinski, P. 1990. Two phase kinetics of the solubilisation in reversed micelles. *Journal of Colloid and Interface Science*, 136(2): 338-351.

Potapov, V.V., Khisamutdinov, R.A., Murinov, Y.I., Baeva, A.L., Ulendeeva, A.D. and Lyapina, N.K.2001. Extraction of Palladium(II) and Platinum(IV) from Hydrogen Chloride Solutions with 3,7-Dimethyl-5-thianonane-2,8-dioneand Complexation of This Reagent with the Platinum Metals, *Journal of Applied Chemistry,*74(7): 1098-1102.

Rajasimman, M., Sangeetha, R. and Karthik, P. 2009. Statistical optimisation of process parameters for the extraction of chromium (IV), from pharmaceutical wastewater by emulsion liquid membrane. *Chemical Engineering*, 150(2-3): 275-279.

Ritcey, G.M. and Ashbrook, A.W.1984. *Solvent extraction principles and application to process Metallurgy, part 1*. Amsterdam: Elsevier, 76.

Sekine, T. and Hasegawa, Y., edited by Hasegawa, Y. 1977. *Solvent extraction chemistry: Fundamentals and applications.* New York: Marcel Dekker, 919.

Shizuka, K., Baba, Y., Inoue, K., Wada, F. and Matsuda, T. 1990. Solvent extraction of palladium (II) and platinum (IV) with N, N - dioctylsuccinamic acid from aqueous chloride media. *The Chemical Society of Japan*, 63:221-226.

Sudderth, R.B. and.Kordosky, G.A.1986. Some practical considerations selection of solvent in the evaluation and selection of solvent extraction reagents, in *Chemical Reagents in the Mineral Industry* edited by Malhotra and Riggs. S.M.E. Littleton Colorado: 181-196.

Suzuki, T.M. and Matsunaga, H.1991. Metal selective polymer resins for the separation and concentration of rare metals. *Trends in Inorganic Chemistry*, 2: 33-47.
Treybal, R.E. 1963. *Solvent extraction*. Second edition. USA: McGraw-Hill.

Warshawsky, A. 1987. Extraction of platinum group metals by ion exchange resins. *In ion exchange and separation processes in hydrometallurgy*, edited by M. Streat and D. Naden. New York: John Wiley and Sons, 127-165.

Wenwei He, wuping Liao, Weiwei Wang, Deqian Li and Chunji Niu. 2008. Mass transfer kinetics of neodymium (III) extraction by calyx [4] arene carboxylic acid using a constant interfacial area cell with laminar flow, *Chemical Technology and Biotechnology,* 83: 1314-1320.

Zhen-ning, L., Ying, X., Jun-jun, S., Wei-jun, S., Guang-xi, H., Zhi-qiang, X. and Yu-xia, K. 2010. Kinetics and mechanism of Re extraction and separation from Mo with trialkyl amine. *Transaction of Nonferrous Metals Society of China,* 20:10-14

APPENDIX A: CHARACTERISTICS OF CYANEX 921 AND KEROSENE

APPENDIX A. 1: Cyanex 921 characteristics

Appearance	Off-white, waxy solid
Specific gravity at 25°C	0.88
Specific gravity at 61°C	0.84
Melting point °C	47-52
Viscosity at 55°C	15.0 cp (15.0 mPa.s
Brookfield viscometer at 100°C	5.5 cp (5.5 mPa.s)
Structure	R_3PO

APPENDIX A. 2: Kerosene characteristics

Appearance	Pale yellow or water - white, mobile oil liquid
Solubility	Insoluble in water
Density	Ca. 0.80
Boiling point	175-325°C

APPENDIX B: EXTRACTION RATIO AND LOADING OF EXTRACTANT

APPENDIX B.1: Extraction Ratio C(t)/C(i) over a period of time

Time (s)	***Test 1***	***Test 2***	***Test 3***	***Test 4***	***Test 5***	***Test 6***	***Test 7***	***Test 8***
0	1	1	1	1	1	1	1	1
300	0.92	0.95	0.98	0.95	0.95	0.96	0.89	0.88
600	0.84	0.90	0.97	0.94	0.93	0.95	0.79	0.82
1200	0.73	0.79	0.93	0.92	0.90	0.94	0.65	0.68
2400	0.66	0.72	0.88	0.90	0.86	0.90	0.57	0.57
5400	0.66	0.71	0.86	0.90	0.86	0.89	0.54	0.51
10 800	0.66	0.68	0.85	0.89	0.86	0.89	0.51	0.49

APPENDIX B.2: Loading of extractant over a period of time

Time (s)	*Test 1*	*Test 2*	*Test 3*	*Test 4*	*Test 5*	*Test 6*	*Test 7*	*Test 8*
0	0	0	0	0	0	0	0	0
300	20.97	26.37	5.31	17.28	22.23	8.46	25.38	57.51
600	35.55	46.53	7.38	26.37	32.13	8.46	44.41	89.55
1200	69.66	108.27	16.38	33.3	44.73	14.13	81	158.04
2400	88.65	143.1	26.91	40.05	59.58	22.41	99.18	244.71
5400	89.19	149.31	32.49	41.94	60.03	24.03	106.38	244.71
10 800	89.73	160.74	33.48	42.84	61.02	24.21	111.96	253.89

APPENDIX C: THE EFFECT OF THE DISTRIBUTION RATIO ON PARAMETERS (PH, *CYANEX 921* CONCENTRATION, TEMPERATURE AND INITIAL PLATINUM CONCENTRATION)

Appendix C.1: The effect of log [H^+] on the log distribution ratio

log [H^+]	***298 k, 2% (V/V), 25.26 mg/L***	***318 K, 2% (v/v), 25.26 mg/L***	***298 K, 8% (v/v), 25.26 mg/L***	***298 K, 2% (v/v), 56.36 mg/L***
-1	0.67	0.61	0.97	0.68
-1.5	0.46	0.41	0.73	0.47
-1.75	0.3	0.26	0.54	0.33
-2	0.04	0.03	0.19	0.33

Appendix C.2: The effect of log *Cyanex 921* concentration on the log distribution ratio

[Cyanex 921]	***298 K, pH 1, 25.26 mg/L***	***318 K, pH 1, 25.26 mg/L***	***298 K, pH 1, 56.36 mg/L***	***298 K, pH 2, 25.26 mg/L***
0.03	0.67	0.61	0.68	0.04
0.6	0.8	0.75	0.8	0.1
078	0.89	0.85	0.9	0.15
0.97	0.97	0.94	0.97	0.19

Appendix C.3: The effect of temperature on the log distribution ratio

Temperature (K)	*pH 1, 2% (v/v), 25.26 mg/L*	*pH 1, 8% (v/v), 25.26 mg/L*	*pH 2, 2% (/v), 25.26mg/L*	*pH 1, (2% v/v), 56.36 mg/l*
298	0.67	0.97	0.04	0.68
303	0.66	0.96	0.04	0.67
308	0.64	0.95	0.04	0.65
313	0.63	0.94	0.03	0.64
318	0.61	0.94	0.03	0.82

Appendix C.4: The effect of log initial platinum concentration on the log distribution ratio

[Pt] (mg/L)	*298 K, pH 1, 2% (v/v)*	*318 K, pH 1, 2% (v/v)*	*298 K, pH 1, 8% (v/v)*	*298 K, pH 2, 2% (v/v)*
1.4	0.67	0.61	0.97	0.04
1.52	0.68	0.61	0.97	0.04
1.61	0.68	0.61	0.97	0.03
1.69	0.68	0.62	0.97	0.03
1.75	0.68	0.62	0.97	0.03

APPENDIX D:THERMODYNAMIC AND KINETICS PARAMETERS VALUES

Appendix D. 1: Thermodynamics parameters values

APPENDIX D.1.1: The effect of temperature on the log distribution ratio (log KD – 1000/T) for each test at different parameters

1000/T(K)	***Test 1***	***Test 2***	***Test 3***	***Test 4***	***Test 5***	***Test 6***	***Test 7***	***Test 8***
(1/298)×1000	0.68	0.68	0.19	0.03	0.18	0.04	0.97	0.97
(1/303)×1000	0.67	0.67	0.19	0.03	0.18	0.04	0.96	0.97
(1/308)×1000	0.65	0.65	0.19	0.03	0.18	0.04	0.95	0.96
(1/313)1×000	0.64	0.64	0.18	0.02	0.18	0.03	0.94	0.95
(1/318)×1000	0.61	0.62	0.18	0.02	0.17	0.03	0.94	0.94

APPENDIX D.1. 2: Thermodynamic parameters values

Thermodynamic aspects	***Test 1***	***Test 2***	***Test 3***	***Test 4***	***Test 5***	***Test 6***	***Test 7***	***Test 8***
ΔH° (kJ/mol)	-5.92	-5.77	-0.85	-1.22	-0.86	-1.20	-2.91	-2.87
ΔS° (J/mo.K)	-6.92	-6.24	0.80	-3.46	0.61	-3.20	8.78	9.02
ΔG° (kJ/mol)	-3.85	-3.54	-1.09	-0.19	-0.99	-0.17	-5.34	-5.55
Ea (kJ/mol)	-3.44	-3.13	1.63	1.26	1.78	1.45	-0.26	-0.39

Appendix D.2: Kinetics parameters values for each experiment

Test	*Flux, J_{aq} (mg/mm^2)*	*Diffusion forward rate constant,10^{-3} δ_f (mm/s)*
1	8.75×10^{-8}	8.77×10^{-3}
2	1.57×10^{-7}	8.77×10^{-3}
3	3.26×10^{-8}	8.77×10^{-3}
4	4.18×10^{-8}	8.77×10^{-3}
5	5.95×10^{-8}	8.77×10^{-3}
6	2.36×10^{-8}	8.77×10^{-3}
7	1.09×10^{-7}	8.77×10^{-3}
8	$2.47\times\times 10^{-7}$	8.77×10^{-3}

APPENDIX E: CONDITIONS FOR THE HALF FACTORIAL EXPERIMENTAL DESIGN

Test 1

Conditions:

pH: 1
Range of contact time in minutes: 0, 300, 600, 1200, 2400, 5400, 10 800 s
Cyanex 921 concentration: 2 mL
Temperature: 298 K
Diluent volume: 98 mL
Aqueous phase volume: 900 mL
Stirring speed: 76.2 rpm
Initial platinum concentration: 28.96 mg/L

Time (s)	***Platinum concentration (mg/L)***
0	28.96
300	26.63
600	24.29
1200	21.22
2400	19.11
5400	19.05
10 800	18.99

Test 2

Conditions:

pH: 1
Range of contact time in seconds: 0, 300, 600, 1200, 2400, 5400, 10 800 s
Cyanex 921 concentration: 2 % (v/v)
Temperature: 318 K
Diluent volume: 98 mL
Aqueous phase volume: 900 mL
Stirring speed: 76.2 rpm
Initial platinum concentration: 56.36 mg/L

Time (s)	***Platinum concentration(mg/L)***
0	56.36
300	53.58
600	50.53
1200	44.33
2400	40.46
5400	39.77
10 800	38.50

Test 3

Conditions:

pH:	2
Range of contact time in seconds:	0, 300, 600, 1200, 2400, 5400, 10 800 s
Cyanex 921 concentration:	2% (v/v)
Temperature:	298 K
Diluent volume:	92 mL
Aqueous phase volume:	900 mL
Stirring speed:	76.2 rpm
Initial platinum concentration:	25.32 mg/L

Time (s)	***Platinum concentration (mg/L)***
0	25.32
300	24.73
600	24.50
1200	23.50
2400	22.33
5400	21.71
10 800	21.60

Test 4

Conditions:

pH: 2
Range of contact time in seconds: 0, 300, 600, 1200, 2400, 5400, 10 800 s
Cyanex 921 concentration: 2%(v/v)
Temperature: 298 K
Diluent volume: 98 mL
Aqueous phase volume: 900 mL
Stirring speed: 76.2 rpm
Initial platinum concentration: 44.46 mg/L

Time (s)	***Platinum concentration(mg/L)***
0	44.46
300	42.54
600	41.85
1200	41.02
2400	40.01
5400	39.80
10 800	39.70

Test 5

Conditions:

pH: 2
Range of contact time in minutes: 0, 300, 600, 1200, 2400, 5400, 10 800 s
Cyanex 921 concentration: 8% (v/v)
Temperature: 318 K
Diluent volume: 92 mL
Aqueous phase volume: 900 mL
Stirring speed: 76.2 rpm
Initial platinum concentration: 47.77 mg/L

Time (s)	*Platinum concentration (mg/L)*
0	47.77
300	45.30
600	44.20
1200	42.80
2400	41.15
5400	41.10
10 800	40.99

Test 6

Conditions:

pH:	2
Range of contact time in minutes:	0, 300, 600, 1200, 2400, 5400, 10 800 s
Cyanex 921 concentration:	2% (v/v)
Temperature:	318 K
Diluent volume:	98 mL
Aqueous phase volume:	900 mL
Stirring speed:	76.2 rpm
Initial platinum concentration:	25.26 mg/L

Time (s)	*Platinum concentration (mg/L)*
0	25.26
300	24.32
600	24.08
1200	23.69
2400	22.77
5400	22.59
10 800	22.57

Test 7

Conditions:

pH:	1
Range of contact time in minutes:	0, 300, 600, 1200, 2400, 5400, 10 800 s
Cyanex 921 concentration:	8% (v/v)

Temperature:	318 K
Diluent volume:	92 mL
Aqueous phase volume:	900 mL
Stirring speed:	76.2 rpm
Initial platinum concentration:	25.43 mg/L

Time (s)	***Platinum concentration (mg/L)***
0	25.43
300	22.61
600	20.12
1200	16.43
2400	14.41
5400	13.61
10 800	12.99

Test 8

Conditions:

pH:	1
Range of contact time in minutes:	0, 300, 600, 1200, 2400, 5400, 10 800 s
Cyanex 921 concentration:	8% (v/v)
Temperature:	298 K
Diluent volume:	92 mL
Aqueous phase volume:	900 mL
Stirring speed:	76.2 rpm
Initial platinum concentration:	55.22 mg/L

Time (s)	***Platinum concentration (mg/L)***
0	55.22
300	48.83
600	45.13
1200	37.66
2400	31.35
5400	28.03
10 800	27.01