SOLVENT EXTRACTION OF RHODIUM FROM CHLORIDE SOLUTIONS IN THE PRESENCE OF $SnCl_2$ WITH KELEX 100™

by

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En remerciement à toutes les femmes que j'admire, et en particulier,

à France, pour sa force qui m'inspire et m'impressionne,
aux Laurences, qui m'ont ouvert l'esprit et les horizons,
à Line, pour sa bontée, générositée et integritée,
et à Maman, qui a su nous donner plus que possible.

Et en souvenir des victimes du 6 décembre, 1989...

ABSTRACT

The aim of this work was to devise and investigate a solvent extraction system for rhodium, from aqueous chloride solutions, having potential industrial applicability. The extractant investigated was Kelex 100, a commercially available derivative of 8-hydroxyquinoline. Ultimately, two different systems were developed. Both are based on an initial complexation reaction between the aqueous rhodium chloride complexes, $[RhCl_{6-n}(H_2O)_n]^{(3-n)-}$ and stannous chloride, referred to as the activation stage, but the two systems use a different Sn:Rn molar ratio. In both cases, the Rh-Sn complexes, either $[Rh(SnCl_3)_5]^{4-}$ or $[RhCl_3(SnCl_3)_3]^{3-}$, respond well to extraction with Kelex 100. One of the main differences between the two systems is in the stripping medium which is used to transfer the rhodium from the loaded organic phase back into an aqueous phase. In the case of the high Sn:Rh ratio feeds, the stripping stage is based on sulfuric acid, whereas in the case of low Sn:Rh ratio feeds, the rhodium is stripped from the organic phase using a sulfite containing hydrochloric acid solution.

The two systems were characterized in terms of their equilibrium and kinetic behaviour during all three stages; activation, extraction, and stripping. Activation was found to proceed either at room temperature or at elevated temperatures and the above-mentioned expected Rh-Sn complexes were identified through ^{119}Sn NMR and Raman spectroscopy. The extraction stage was found to be quantitative for rhodium and it was also found to be very rapid, with contact times of less than five minutes sufficient for rhodium extraction. The extraction mechanism was determined to be ion-pair formation with the protonated Kelex 100 molecules at a stoichiometry such that the overall charge in the organic phase is neutral, i.e., three Kelex 100 molecules for $[RhCl_3(SnCl_3)_3]^{3-}$ and four for $[Rh(SnCl_3)_5]^{4-}$.

The stripping stages were the most problematic for both systems. In one case, the system was eventually abandoned due to limitations in the amount of rhodium which could be transferred to the sulfuric acid strip solution. For the low Sn:Rh system, reasonable rhodium transfer and concentration level were obtained. The rhodium complex in the strip solution has been proposed to be $[RhCl_2(SO_3)]^{3-}$. Strip solutions up to 4×10^{-2}M in rhodium concentration have been produced, from inital feed solutions having a rhodium concentration of about 4×10^{-3}M. Preliminary flowsheets are proposed for further refinement for both systems, although only the second system, the low Sn:Rh ratio system which uses sulfite stripping, is advocated for further development.

RESUME

Le but de cette étude était de développer un système d'extraction par solvant pour le rhodium, à partir de solution aqueuse de chlorure. L'extractant utilisé était le Kelex 100, un dérivé du 8-hydroxyquinoline, qui est disponible commercialement. Deux systèmes différents ont été developpés. Ces deux systèmes sont basés sur une réaction de complexation entre les complexes de chlorures du rhodium, $[RhCl_{6-n}(H_2O)_n]^{(3-n)-}$, et le chlorure d'étain (stanneux), mais les deux systèmes utilisent un ratio molaire de Sn:Rh différent. Dans les deux cas, les complexes Rh-Sn formés, soit $[Rh(SnCl_3)_5]^{4-}$ et $[RhCl_3(SnCl_3)_3]^{3-}$, répondent bien à l'extraction avec le Kelex 100. Une des principales différences entre les deux systèmes est la solution de réextraction qui est utilisée pour transférer le rhodium de la phase organique à une nouvelle phase aqueuse. Dans le cas des solutions d'alimentation qui utilisent un ratio molaire élevé de Sn:Rh, la solution de réextraction est de l'acide sulfurique et dans l'autre cas, le rhodium est réextrait à l'aide d'une solution de sulfite de sodium dans de l'acide chlorhydrique.

Les systèmes ont été étudiés en fonction de leur cinétique, ainsi que leurs réponses à l'équilibre, pour les trois parties du système: l'activation, l'extraction et la réextraction. Il a été trouvé qu'il est possible d'activer la solution de rhodium avec le chlorure d'étain (stanneux) soit à la température de la pièce, soit à une température plus élevée. Les complexes Rh-Sn obtenus ont été identifiés par spectroscopie Raman et par la RMN ^{119}Sn. Il a été determiné que le mécanisme d'extraction se fait par paires d'ions avec le Kelex 100 protoné, à une stoichiométrie telle que la solution organique maintient une charge neutre, i.e. trois molécules de Kelex 100 pour $[RhCl_3(SnCl_3)_3]^{3-}$ et quatre pour $[Rh(SnCl_3)_5]^{4-}$.

La partie de réextraction a été la plus problématique pour les deux systèmes. Dans un cas, le système a dû être abandonné à cause de limitation dans la quantité de rhodium qui pouvait être transféré à la solution de réextraction, l'acide sulfurique. Dans le second cas, un transfert de rhodium acceptable a été obtenu. Le complexe de rhodium qui existe dans la solution de réextraction à base du sulfite de sodium a été proposé comme étant $[RhCl_2(SO_3)_2]^{3-}$. Des solutions de réextraction contenant jusqu'à $4x10^{-2}$M rhodium ont été produites à partir de solution mères contenant $4x10^{-3}$M rhodium. Des schémas préliminaires sont proposés pour les deux systèmes, mais il est suggeré que de plus amples développements soit consideré seulement pour le systeme basé sur la réextraction avec la solution de sulfite de sodium.

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NOMENCLATURE

I	ionic strength
α	activity
K	stability constant
β	overall stability constant
k	rate constant
k_{obs}	observed rate constant
$D_{Rh,X}$	distribution coefficient for rhodium extraction
$D_{Rh,S}$	distribution coefficient for rhodium extraction
r	rate
r^2	square of the linear correlation coefficient
T	temperature
min	minute
CT	contact time
org	organic phase
aq	aqueous phase
overbars	organic phase species

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CHAPTER 1

INTRODUCTION

Rhodium, Rh, belongs to the family of platinum group metals (PGM) along with platinum, palladium, ruthenium, osmium and iridium. These elements normally occur together in nature, and therefore, it is necessary to separate them in order to produce pure, saleable metals. Because of the high value of these elements, the methods used to refine them tend to be kept secret, and it is also likely that much of the research which is carried out on novel refining techniques is never made public. Nevertheless, it is generally agreed upon that satisfactory separation schemes have been developed for most PGM, but not for rhodium [1].

The purification and recovery of rhodium from chloride solutions has always been problematic due mainly to the complex aqueous chemistry of rhodium in such solutions. While significant improvements in process technology have been achieved in the past twenty years for most PGM, rhodium, because of its peculiar aqueous chemistry, has defied most straightforward modern recovery techniques, such as solvent extraction and ion exchange. Rhodium forms mixed aquo-chloro complexes in chloride solutions which can be quite inert and which do not respond well to solvent extraction. Rhodium is therefore still separated from the base metals, once all of the other PGM have been recovered, through a classical purification method based on numerous precipitation-dissolution steps [2].

During the past ten years, a growth in demand for rhodium, due to the increasing use of Pt/Pd/Rh-containing catalytic converters in car exhaust systems, has prompted significant research activity on replacing this outdated technique. A clear indication that the technique should be improved was the dramatic price increase from \$2000 to \$7000 US (per ounce) in the fall of 1990 due to process/plant problems at the South African producer, Matthey Rustenburg Refiners (now Precious Metals Refiners). The other rhodium producers were not able to fill the market void, because of the long turn-around time of this process, causing a temporary shortage of rhodium and buyer panic. The price of rhodium at present (April 1996) is \$320 US (per ounce). Given the high value of the metal and the outdated technology used for its refining, it is clear that the study of the intricate chemistry of Rh(III) chloride solutions and the possible development of a modern process for its separation is highly desirable.

The focus of this work was to study the aqueous chemistry of rhodium(III) from chloride solutions and to then try to develop a solvent extraction system for rhodium recovery with the potential of finding industrial application. Because it has been clearly established, in the literature[1], that direct, conventional solvent extraction is not possible for rhodium, solvent extraction was coupled with the use of $SnCl_2$ to alter the aqueous chemistry of rhodium and render it extractable. Preliminary work leading to the identification of such a separation system was described in an M.Eng. thesis [3] by the present author. This system was based on the activation of the rhodium chloride feed solution with $SnCl_2$ using a high ratio of Sn(II):Rh (at least twelve) followed by extraction using Kelex 100[2] and multiple cross-current stripping with concentrated H_2SO_4-Na_2SO_4 solutions [4]. Further work carried out on the high Sn:Rh system, described in Chapter 4, eventually led to the realization that this process could not respond to industrial demands. A second solvent extraction system was then developed, based on activation with a lower Sn:Rh ratio followed by extraction with Kelex 100 and stripping with Na_2SO_3. This system is reported in Chapters 5 and 6.

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[1] A review of the chloride solution chemistry of rhodium, the present-day recovery methods, and some previous solvent extraction studies is presented in Chapter 2.

[2] Proprietary product of WITCO Chemical Co.

In summary, both of the systems designed can be divided into three main sections which include (i) rhodium feed pretreatment, referred to as activation, (ii) extraction, and (iii) stripping. More specifically, the activation stage consists of the addition of $SnCl_2$ to the rhodium chloride feed to render rhodium extractable. One of the main differences between the two systems is in the amount of tin required. The activated feed is then subjected to a conventional solvent extraction procedure with direct extraction, possibly followed by a scrubbing stage, and finally, stripping. Both of the systems have been developed for the extractant Kelex 100, which is a 7-substituted derivative of 8-hydroxyquinoline.

The next stage for both systems is the stripping stage where the Rh is transferred from the organic phase back to an aqueous solution. Depending on the Sn:Rh ratio used during the activation stage, the loaded organic can be stripped with either sulfuric acid or a sulfite solution. The identification and chemical characterization of the complexes involved in the two stripping reactions were carried out and are described in Chapters 4 and 5, respectively. The final stage consists in the regeneration of the organic phase, which includes tin removal followed by an acid wash.

For clarity, the results are separated into two main parts. Following the literature review in Chapter 2 and a brief description of the experimental procedure in Chapter 3, the rhodium solvent extraction system designed for high Sn:Rh ratio feeds (> 6:1) is presented in Chapter 4. The second system, which has been designed for low Sn:Rh feeds (< 6:1), is presented in Chapter 5. Each of these Chapters (4 and 5) is subdivided into three main parts representing the activation, extraction and stripping stages. Chapter 6 is dedicated to the kinetics of the stripping reaction of the low Sn:Rh solvent extraction system. Finally, in Chapter 7, the work is completed with a summary of the most important findings and a recommendation for possible future work.

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CHAPTER 2

LITERATURE REVIEW

2.1 INTRODUCTION

Rhodium and the other PGM occur together in nature, as well as with silver and gold, either as native alloys in placer deposits, or in lode deposits where they are associated with copper and nickel [1]. Originally, the PGM were recovered after dissolution in oxidizing chloride liquors through a cumbersome series of precipitation-dissolution steps adopted from analytical chemistry techniques [2,3]. This was the most common method until about the mid-1970s, at which point the major refining companies modernized their processes by implementing more efficient separation techniques such as solvent extraction and, to a lesser degree, ion exchange, for most of the PGM, but not for rhodium. Although rhodium complexes are considered to be relatively labile in comparison to some of the other PGM [4], the failure in achieving a modern process for rhodium lies in its particular chemistry in chloride solutions. The type of complexes formed rendered this otherwise straight-forward goal difficult and to date, no industrial solvent extraction process has been published for rhodium, although it is true that research in this area is usually very well guarded.

2.2 AQUEOUS RHODIUM CHLORIDE CHEMISTRY

2.2.1 Aqueous Chloride Solutions

Rhodium can exhibit a number of oxidation states but the two most usual ones are I and III with the III complexes being more common in chloride solutions. A number of different complexes are formed in such solutions, but contrary to many other transition metals, rhodium does not exist simply as chloro complexes, $[RhCl_n]^{(n-3)-}$, but rather it forms mixed aquo/chloro complexes [5] such as $[RhCl_{6-n}(H_2O)_n]^{(n-3)-}$. The failure in developing an industrial solvent extraction process has been attributed to the physical characteristics of the aquo complexes [3]. H_2O, like Cl^-, is in the inner coordination sphere of the rhodium cation and therefore acts as a ligand and not simply as water of hydration [4]. In addition, the aquated complexes have been found to be more inert than is the non-aquated hexachlororhodate complex, $[RhCl_6]^{3-}$. The aquated (and most probably, very hydrated) complexes cannot be extracted into an apolar organic solvent since they are quite hydrophillic, nor are they as likely as $RhCl_6^{3-}$ to undergo chemical reactions.

The aquation reaction can be represented, starting with $[RhCl_6]^{3-}$, by substitution reactions as follows:

$$[RhCl_6]^{3-} + H_2O \rightarrow [RhCl_5(H_2O)]^{2-} + Cl^- \qquad (2.1)$$

$$[RhCl_5(H_2O)]^{2-} + H_2O \rightarrow [RhCl_4(H_2O)_2]^{-} + Cl^- \qquad (2.2)$$

...

$$[RhCl(H_2O)_5]^{2+} + H_2O \rightarrow [Rh(H_2O)_6]^{3+} + Cl^- \qquad (2.3)$$

The species existing in solution can therefore range from the fully aquated hexaaquorhodate, $[Rh(H_2O)_6]^{3+}$, to hexachlororhodate, $[RhCl_6]^{3-}$ with the mixed aquo/chloro complexes, $[RhCl_{6-n}(H_2O)_n]^{(n-3)-}$, also co-existing in solution. The abundance of each complex depends primarily on the chloride ion and water activities. Hydrolysis complexes are also believed to occur at acidities below 0.1M H^+[4], resulting in complexes such as $[RhCl_5(OH)]^{3-}$. To further complicate the situation, there has also been speculation about Cl- and O-bridged polymeric-type rhodium complexes in literature [5,6,7]. The existence of these complexes has yet to be proven and little interest has been shown in them in recent years.

2.2.2 Speciation

Although the aquation of $[RhCl_6]^{3-}$ is well established [5,8,9,10], no consensus has been reached with regards to the exact speciation of these complexes in solution. In terms of developing an ion (liquid or solid) exchange process for rhodium, it is important to know both the specific complexes present in solution and their relative abundance, since cationic, anionic and neutral species are extracted via different mechanisms, and with different types of extractants or resins. Only by knowing the speciation is it then possible to choose an appropriate reagent. A speciation diagram for Rh-Cl would be useful for obtaining such information, but although such diagrams are well established and accurate for many elements, the lack of reliable and reproducible thermodynamic data for the Rh-Cl system has resulted in confusion as to the exact speciation.

One attempt at deriving a speciation diagram for the complexes ranging from $[RhCl_6]^{3-}$ to $[Rh(H_2O)_6]^{3+}$ was made by Cozzi and Pantani [11], who based their diagram on stability constants obtained from polarographic data. Their diagram is reproduced in Figure 2.1. In the original version, the x-axis was denoted as a_{Cl^-} but through recalculation of their data, it would appear that they really refer to mean HCl activity ($\alpha_{\pm(HCl)}$).

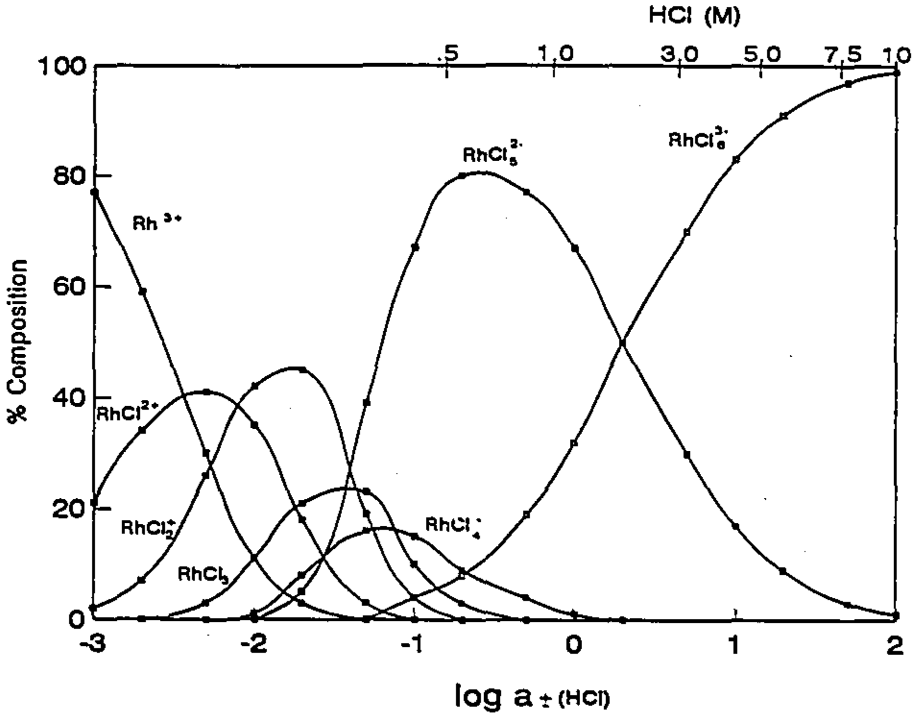

Figure 2.1: Rhodium-chloride speciation after Cozzi and Pantani [11]

Because of considerable deviations between concentrations and activities at high chloride ion concentrations, a HCl concentration scale is also included in Figure 2.1 for more direct application of the diagram to real solutions. Conversion of $\alpha_{\pm(HCl)}$ to HCl concentration was made on the basis of the data published by Robinson and Stokes [12]. The constants calculated by Cozzi and Pantani, along with the other published stability constants are summarized in Table 2.1. Clearly, there are only limited stability constant data available in the literature for rhodium chloride complexes and even those which are available are often inconsistent. It should be mentioned that another group, Mihailov et al [13] has also published a speciation diagram, however, it is no longer considered valid [3,14]. This is because only five stability constants are given for six different complexes and therfore, two complexes, ($[RhCl_6]^{3-}$ and $[RhCl_5(H_2O)]^{2-}$) are wrongly considered as equivalent.

Table 2.1: Summary of stability constant data for Rh(III) chlorocomplexes.

T (K)	Ionic Str (M)	log K						Ref
298	1.0	K_1=2.45	K_2=2.09	K_3=1.38	K_4=1.16	K_5=1.67	K_6=-0.32	11
298	1.0	K_1=2.62	β_2=4.38	β_3=5.94	β_4=7.42	β_5=8.79		13
308	4.0						K_6=-1.1	15
298	0.1				K_4=1.39	K_5=0.55	K_6=-0.23	16
288	4						K_6=-0.72	8
293	4						K_6=-0.82	8
298	4						K_6=-0.93	8
308	4						K_6=-1.14	8
303	4					K_5=0.90		9
308	4					K_5=0.83		9
313	4					K_5=0.80		9
318	4					K_5=0.77		9
348	2.5	K_1=-0.05						17
353	2.5	K_1=-0.10						17
358	2.5	K_1=-0.15						17
291	var						K_6=-0.3	17
393	6.0	K_1>3.0	K_2>3.0	K_3≈3.0	K_4=2.4	K_5=1.4	K_6=-0.25	17

2.2.3. Kinetics of Aquation/Anation and Speciation

Although speciation diagrams are useful, the kinetics of exchange between the chloride ion and water ligands are equally important because this determines whether or not the equilibrium state is easily reached and whether an equilibrium speciation diagram could be applied to typical industrial solutions.

Since industrial liquors from which rhodium are recovered are relatively concentrated in terms of chloride ion, the species most abundant in solution are $[RhCl_4(H_2O)_2]^-$, $[RhCl_5(H_2O)]^{2-}$ and $[RhCl_6]^{3-}$ (Figure 2.1). The rates of aquation (the exchange of a Cl^- ligand by a H_2O ligand) and the rates of anation (the reverse of aquation) for these three complexes are therefore the most important.

A kinetic study has been performed on the aquation/anation of $[RhCl_6]^{3-}$ [8] at 298 K (I=4):

$$RhCl_6^{3-} + H_2O \underset{k_2}{\overset{k_1}{\rightleftharpoons}} RhCl_5(H_2O)^{2-} + Cl^- \qquad (2.4)$$

where $k_1 = 1.1 \times 10^{-1}\ min^{-1}$
$k_2 = 1.3 \times 10^{-2}\ min^{-1}\ M^{-1}$

Similarly, the kinetics of the second reaction have also been studied [9] at 298 K (I=4):

$$RhCl_5(H_2O)^{2-} + H_2O \underset{k_4}{\overset{k_3}{\rightleftharpoons}} RhCl_4(H_2O)_2^- + Cl^- \qquad (2.5)$$

where $k_3 = 2.32 \times 10^{-3}\ min^{-1}$
$k_4 = 2.11 \times 10^{-2}\ min^{-1}\ M^{-1}$

It should be noted that the k_3 and k_4 values given here were calculated using the Arrhenius equation from rate constants reported from 30°C to 45°C [9]. Calculation of the reaction half-lives showed that the aquation of $[RhCl_6]^{3-}$ occurs more rapidly ($t_{1/2} = 4$ min at 4M Cl^-) than that of $[RhCl_5(H_2O)]^{2-}$ ($t_{1/2} = 8$ min at 4M Cl^-). This trend continues as the number of chloride ion ligands decreases. The kinetics also showed that the aquation/anation reactions for the three anionic complexes of rhodium are sufficiently fast that in an industrial solution, equilibrium of the rhodium chloride complexes will be reached and speciation diagrams would therefore be useful.

For comparison reasons, a speciation diagram for Rh-Cl, in pure HCl solutions, using the kinetic values was constructed [14]. For this diagram, the equilibrium state was defined on the basis of the rates of the ligand exchange reactions (at $-d[RhCl_n]/dt = 0$) rather than on the basis of the stability constants of the complexes. Only the three anionic species were considered here, since in solutions of >0.5M Cl^- these three species are believed to predominate (Figure 2.1). Also, since water is one of the reactants (ligands) and since the activity of water is known to be considerably lower than one in concentrated HCl media [18], its influence on the aquation of the $[RhCl_6]^{3-}$ should not be ignored. It therefore seemed worthwhile to calculate a speciation diagram for Rh-Cl in pure HCl solutions using activity rather than concentration terms for water and chloride ion. The activity coefficients of the rhodium species was assumed to be one since no information was available.

In order to calculate the single ion activity of the chloride ion and the water activity, a method proposed by Jansz [19] was used. Having estimated the necessary activity data, the speciation diagram of Figure 2.2 was calculated. The dotted line on the diagram shows the activity of water as a function of HCl concentration. When comparing the speciation diagrams of Figure 2.1 and 2.2, it is clear that the diagrams, overall, show similar trends with the predominance of $[RhCl_6]^{3-}$ at high HCl concentrations. The major difference lies in the predominance area of $[RhCl_5(H_2O)]^{2-}$ which was found to be larger when the ligand exchange kinetics and water and chloride ion activities are used.

From observations on the color of various Rh(III) chloride solutions prepared at different acidities and chloride ion levels [14], and from subsequent studies on the aquation of Rh(III) [20], it may be deduced that the speciation diagram of Figure 2.2 better reflects the reality of solutions similar to those found industrially. As the diagram of Figure 2.2 suggests, in typical refining solutions, 2-5M Cl^-, the aquated rhodium complex, $RhCl_5(H_2O)^{2-}$ is quite prominent and is expected to affect the extraction behaviour of the solution.

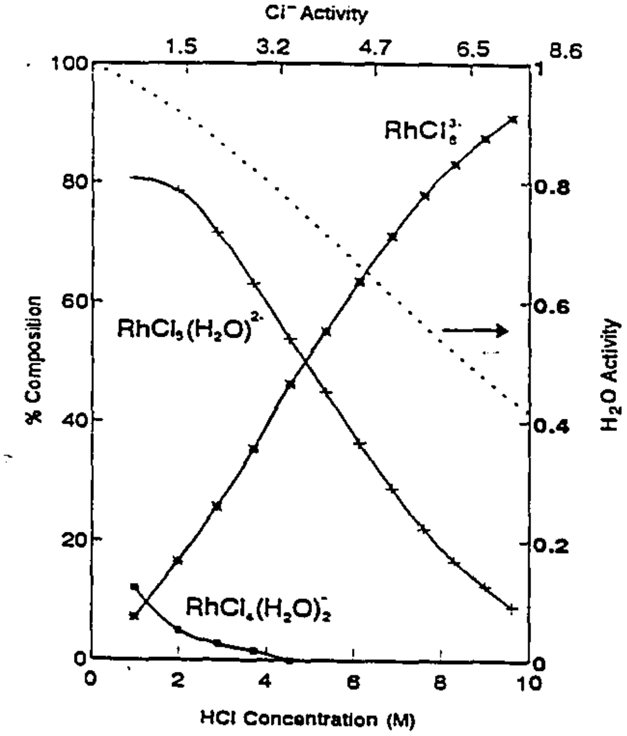

Figure 2.2: Rhodium-chloride speciation diagram for HCl solutions based on ligand exchange rates and on water and chloride ion activities.

2.3 CLASSICAL REFINING OF RHODIUM

The PGM are refined through a variety of techniques and a typical flowsheet for their recovery, such as that used by INCO Ltd. in Acton, U.K., is depicted in Figure 2.3 [3,21,22]. There is some uncertainty as to the method presently used to recover iridium and the two suggested paths are shown in that Figure. As is the case for virtually all PGM recovery flowsheets, rhodium is the last metal processed and it is still recovered through a complicated precipitation technique. As recently as August 1994, it was still reported [23] that the different major rhodium refiners, INCO, Impala, LONRHO and Degussa were all still using precipitation to recover rhodium. It was less clear what process was being used by Matthey Rustenburg refiners (now Precious Metals Refiners), however it was reported that none of their possible processes was without problems.

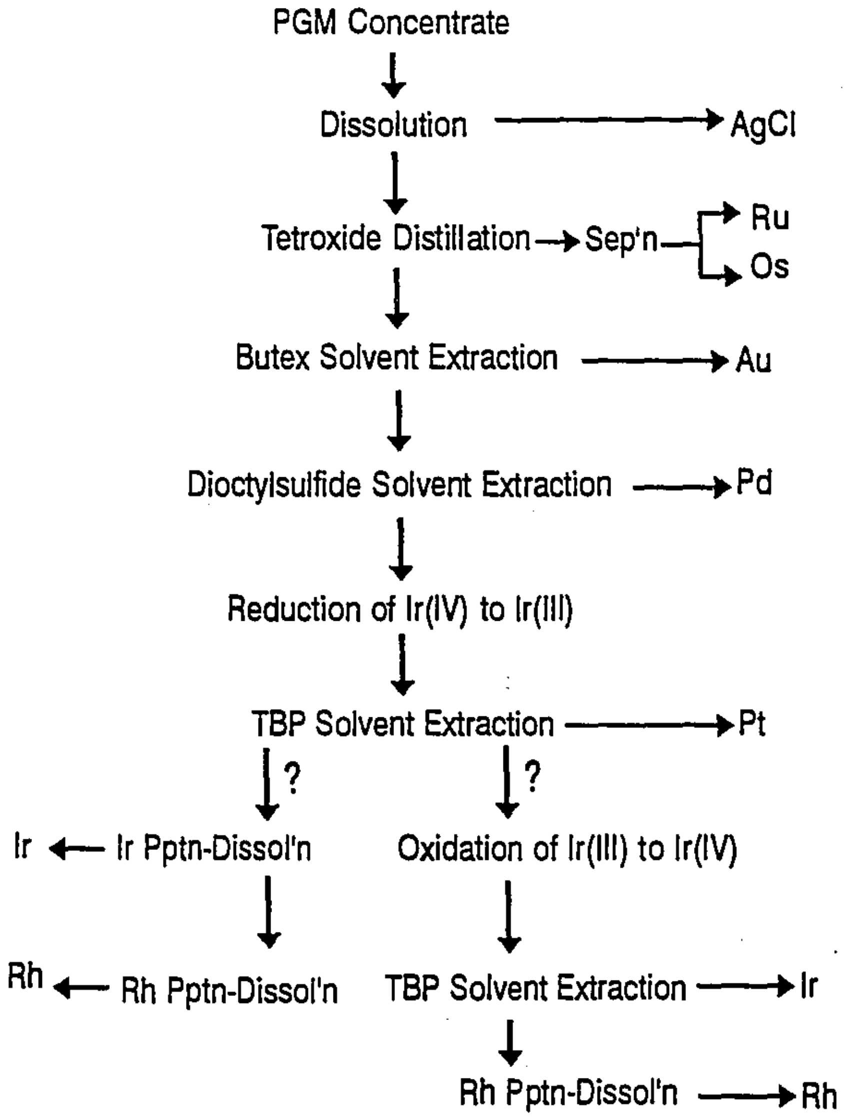

Figure 2.3: INCO precious metals refining flowsheet.

Although it is still used, the precipitation-dissolution scheme for the recovery of rhodium is no longer considered satisfactory because of its numerous drawbacks. It is a lengthy separation process, sometimes involving as long as four to six months internal recycling for the final recovery of pure rhodium metal. The technique is quite tedious since the precipitation must be carried out a number of times in order to ensure that the final product is of acceptable purity and this makes the overall process labour intensive, inefficient and costly. A simplified flowsheet for the rhodium precipitation-purification scheme is shown in Figure 2.4 [3,24].

As depicted in Figure 2.4, the first step of this process involves the formation of the nitrite complex $[Rh(NO_2)_6]^{3-}$ from $RhCl_6^{3-}$. Because this complex is extremely stable to hydrolysis, the impure Rh-containing solution can be subjected to neutralization with caustic soda to precipitate some of the impurities through hydrolysis [3]. After filtration, the rhodium is precipitated with ammonia as $Na(NH_4)_2[Rh(NO_2)_6]$ which is a partially selective precipitation step over the other PGM which may also be present in the rhodium solution. For this precipitation, however, it is important that a high concentration of ammonia be used in order to suppress the solubility of this complex and achieve high rhodium precipitation efficiency. After another filtration, the precipitate is redissolved in HCl and depending on the purity of the solution, the cycle is started over.

It is this cycle of precipitation-dissolution stages that renders the process inefficient and time-consuming. Once the ammonium-nitrite rhodium salt is of acceptable purity, the final dissolution in hydrochloric acid is followed by the precipitation of rhodium with ammonia to give $(NH_4)_3[RhCl_6]$. The last step involves the reduction of rhodium to the metallic state either directly from this salt with formic acid or with $H_2(g)$ at 1000°C [24]. Due to rhodium's high value and significant demand for automobile catalytic converters, there is a definite need to develop a more efficient separation and recovery process for rhodium.

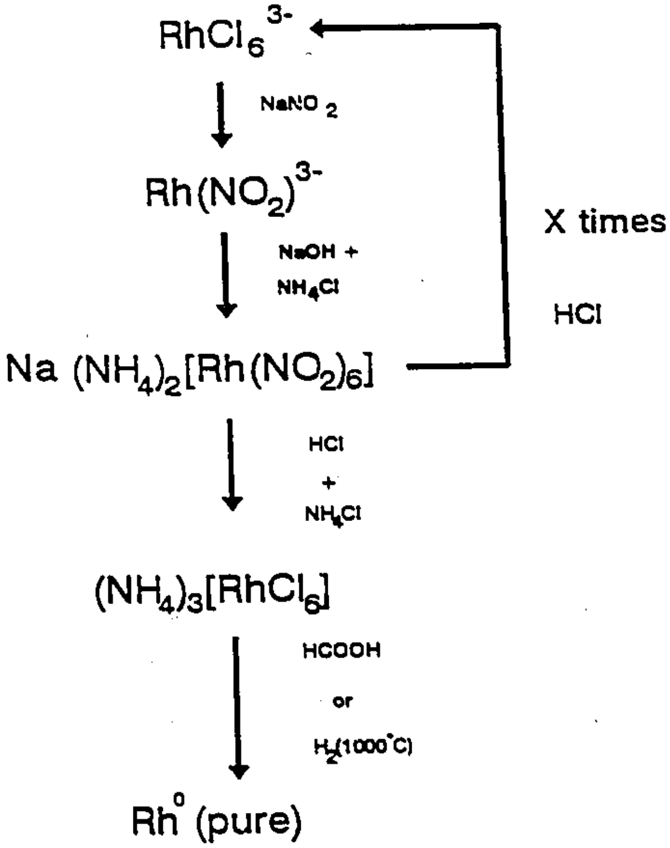

Figure 2.4: Classical rhodium precipitation-purification process.

2.4 DIRECT RHODIUM EXTRACTION FROM CHLORIDE SOLUTIONS

A significant amount of research has focused, in the past, on trying to develop direct solvent extraction systems for rhodium from pure chloride solutions.

Unfortunately, none of the systems tested have proven to be sufficiently attractive to be pursued industrially. Some of the major findings will be briefly reviewed here.

2.4.1 Solvent Extraction of Rhodium with Amines

Given that rhodium forms anionic complexes in typical refining solutions, it was expected that anion exchange extractants, such as amines, should yield the best results and a number of studies with various organic amine extractants [25] have been performed. It was found that although rhodium can in fact be extracted under certain conditions, the other PGM are usually more readily extracted and therefore amines are useful only when rhodium is the only precious metal in solution. Amines are also capable of extracting a number of base metals and, therefore, selectivity can be quite problematic. In general, with amines, the extraction of rhodium was found to be favoured at low acidities and low chloride concentrations, where mixed aquo/chloro and hydroxy/chloro rhodium complexes are expected to predominate. In the platinum metals refining industry, the acidity and chloride concentration of the rhodium feed liquor is usually quite high so direct application of amine extractants would, in fact, be difficult.

Studies performed on the extraction of rhodium with primary [26] and tertiary amines (tri-n-octylamine [27,28] or tri-isobutylamine [25]) have shown that rhodium is only significantly extracted at 0.1M HCl. At HCl concentrations of 1-12M, the extraction drops to zero. Better extraction results are obtained if a quaternary ammonium extractant is used [29,30], however, in this case, stripping becomes very problematic. The inability of the amines to extract at high acidities (and chloride ion concentrations) is not expected if the typical extraction mechanism of amines is considered.

The extraction of precious metals with amines (here the tertiary amine is used as an example) is believed to be generally represented by the following reactions:

$$\overline{R_3N} + HCl \rightleftharpoons \overline{R_3NH^+Cl^-} \qquad (2.6)$$

$$3\overline{R_3NH^+Cl^-} + MCl_6^{3-} \rightleftharpoons \overline{(R_3NH^+)_3 \cdot MCl_6^{3-}} + 3Cl^- \qquad (2.7)$$

Since acid is required for the extraction to proceed (equation 2.6), it is difficult to explain the drop in extraction with increasing acidity, if the acid effect is separated from the chloride effect. The drop in extraction degree with increasing chloride ion concentration might be explained by considering reaction 2.7. The extraction of the precious metal species is based on an anion exchange reaction between chloride and the negative metal complex. If the concentration of chloride ion is too high, then through simple mass effect, its replacement by the metal complex will become increasingly difficult and the extraction degree will drop. In fact, one of the stripping reagents which can be used to strip the precious metals from loaded amines is a concentrated chloride ion solution.

For rhodium, however, the extraction reaction is believed to be more complicated than equation 2.7. It has been speculated that contrary to what is expected for other extractants, the aquated rhodium complex, $[RhCl_5(H_2O)]^{2-}$, can, in fact, be extracted with amines [3,29]. Due to the hydrophilicity of this complex, it does not remain in the organic phase as this species but rather it is believed to undergo rapid dimerization or possibly polymerization such as:

$$2\overline{(R_4N^+)_2 \cdot [RhCl_5(H_2O)^{2-}]} \rightarrow \overline{(R_4N^+)_3 \cdot [Rh_2Cl_9^{3-}]} + \overline{R_4N^+Cl^-} + 2H_2O \qquad (2.8)$$

The $Rh_2Cl_9^{3-}$ anion has been found to be so strongly bound to the organic ammonium cation that it is then "locked-up" in the organic phase and stripping of Rh from quaternary ammonium extractants is not possible.

An investigation of the kinetics of extraction of rhodium from chloride solutions with a quaternary ammonium chloride extractant was performed [31]. The extraction was found to be very fast initially, with the bulk of the extraction occurring within one minute, after which the rate decreased significantly and extraction continued until about fifteen minute contact time. An extraction degree of about 80% was obtained under the best conditions (25°C, $[H^+]$=1M, $[Cl^-]$=1M). The rate was found to decrease with increasing proton and chloride ion concentrations. Also, fresh solutions of Na_3RhCl_6 showed higher overall extraction than did aged solutions; however, the aging time was not specified. Stripping and selectivity were not studied, but, and as mentioned above, these can be expected to be problematic.

Overall, then, it has been shown through the above studies that amines cannot be used as industrial extractants for the direct recovery of Rh from typical refining liquors either because of poor extraction or because of stripping problems.

2.4.2 Solvent Extraction of Rhodium with Other Extractants

Amines are not the only type of extractant which have been investigated and a variety of other extractants, including some unexpected types such as solvating extractants, have been tested for the extraction of rhodium. A very brief overview of the results obtained with these different extractants is given here.

Prior to the start of the investigation on the tin-based solvent extraction systems developed in this work, the direct extraction of rhodium from chloride solutions with 7-substituted 8-hydroxyquinoline derivatives, similar to the commercially available Kelex 100, was studied [32]. Kelex 100 can extract via two different mechanisms; either by chelation or by anion-exchange in acidic solutions [33,34]. It was found that a maximum of only 40% rhodium could be extracted ($4x10^{-3}$M Rh feed solution, 6M HCl, 25°C, and $5,8x10^{-2}$M Kelex 100). Extraction tended to increase with increasing chloride ion concentration and also, to a lesser extent with increasing acidity. This was explained by supposing that the only extractable complex is $RhCl_6^{3-}$ and that it is extracted through ion-pair formation with the protonated extractant. Attempts to let the aqueous solution reequilibrate, i.e., convert the remaining $[RhCl_5(H_2O)]^{2-}$ to $[RhCl_6]^{3-}$ and extract all rhodium as $[RhCl_6]^{3-}$ failed. This was attributed to the continuing aquation even inside the loaded organic phase due to the formation of water-in-oil microemulsions [20].

Another recent study [35] focused on the use of a pyridine derivative (3-(4-pyridyl)1,5-diphenylpentane). Encouraging extraction results were obtained, with up to 85% extraction at 3M HCl, and a reasonably good extraction isotherm was also produced. Selectivity over base metals was good, except for Fe(III) which was highly co-extracted and Ni(II) which was partially co-extracted. The other precious metals were found to be quantitatively co-extracted and these would therefore have to be removed prior to rhodium solvent extraction. The main problem seemed to be stripping which proved to be very difficult. Stripping solutions containing 1M NaOH, 10M HCl, and thiourea were all tried, but quantitative stripping was not possible. (maximum about 50% stripping). It is not known whether work on this system has progressed further, but it would appear that, to date, this may be the most promising direct rhodium solvent extraction system. However, the stripping problems must be overcome if this is to attract further industrial interest.

The use of pyridine derivatives for the extraction of rhodium was tested previously to the above study [36]. Rhodium extraction was found to be favoured at chloride concentrations greater than 3.7M, suggesting that the $[RhCl_6]^{3-}$ complex is extracted. Most interesting, however, was the finding that the addition of hypophosphorous acid to the feed solution dramatically improved extraction. It is believed that the rhodium complexes were reduced to Rh(I) complexes which are more easily extracted. The reaction between hypophosphorous acid and rhodium was not described but hypophosphorous acid was proposed as a possible industrially attractive labilizing agent for rhodium. A study of the stripping stage was not performed and therefore, at that stage of the study, a solvent extraction system could not be proposed, nevertheless, the use of hypophosphorous acid as labilizing agent is an interesting observation.

Because of the large number of systems which have been attempted but which gave, overall, negative results in terms of industrial applicability, a concise summary of the various studies is considered sufficient and is presented in Table 2.2 below.

Methylisobutyl ketone (MIBK) was also studied as extractant for rhodium from 6M HCl solutions, however, a pretreatment step was required [37] and therefore, this is not really a direct rhodium solvent extraction system. Ammonium pyrrolidine dithiocarbamate was added to the rhodium feed. In this case, up to 80% extraction was achieved but all of the other PGMs and a number of important base metals, such as Cu, Ni, As, Fe, Sn and As, are also co-extracted. Stripping was not studied. This study would seem to be more applicable as a preconcentration step rather than as a selective solvent extraction system.

A rather active search for synergistic systems for rhodium extraction has also been underway in the past ten years. One system recently studied [38] involved the common extractant trioctylamine with the much less common 2-mercaptobenzothizole. The system only works at very low acidity, 0.01M HCl, and also needs very long contact times (4 hours). The authors mention that their solutions contain only about 5 ppm rhodium, which seems to be too low to be very accurate when using atomic absorption analysis, as they have reported. The rhodium complex existing in the organic phase was described as $Rh.(MBT)_2.TOA.Cl$. Selectivity and stripping were not tested, but in any case, 0.01M HCl solutions are not representative of industrial refining liquors.

Table 2.2: Summary of rhodium solvent extraction systems (X = extraction, CT = contact time)

Extractant (and Aqueous Medium)	General Comments	Ref
Di-n-heptyl sulfoxide [DHSO] in 1,1,2 trichloroethane (6M HCl)	Max 60% X (CT=40 min). Not selective. Strip with 0.7M $NaNO_2$ at 70°C at pH=7.	39
Tributyl phosphate [TBP] (HCl 1-9M)	Max of 16% X only.	40
Trioctyl phosphine oxide [TOPO] (0.01 to 10M HCl)	40% X at 0.05M HCl (but only 10% at 1M HCl).	41
Dinonylnaphthalene sulfonic acid in n-heptane (Weak HCl)	Liquid cation exchanger. 90-95% recovery. Good selectivity, except for Ru. Strip with 6M HCl.	42
Mono-N-amide [RHNCOR'] (Strong HCl)	For Ir X over Rh (III). No Rh X.	43
Dioctyl acetamide (0.1M to 9M HCl)	75% X at 0.1M HCl, but no X at > 1M HCl. Not selective over PGMs.	44
1,5 diphenyl formazans (0.1M HCl)	No Rh X.	45
thiadiazole-2-nonylmercapto-5-thiol (1-5M HCl)	< 10% X.	46

Clearly, then, much of the scoping work for the direct extraction of rhodium from chloride solutions has already been done with no encouraging results. In some cases, it could easily have been predicted that the attempted extractant would fail, but the pressing need to identify a system, the frustrating results, and the specific chemistry of rhodium in chloride solutions, was such that researchers often decided to simply try all available extractants. The abundance of negative results for the direct extraction of rhodium from chloride solutions does suggest that other avenues should be considered.

2.4.3 Ion Exchange of Rhodium in Chloride Solutions

Two review articles, intended for analytical chemists, describe the separation of rhodium from the other PGMs using ion exchange (IX) techniques [10,47]. There has been some work carried out with IX in the hope of developing a system for industrial rhodium recovery applications. In fact, it has been reported that Matthey Rustenburg Refiners may be using an IX process in their rhodium recovery operations [22], although details have not been published and it is not clear whether the IX process is actually being used.

As with solvent extraction, most IX systems which can extract rhodium also extract other PGM, and therefore they can only really be used effectively if no other PGM are present in solution. Some of the resin types which have been investigated include strong base anion exchange resins [47,22], thiourea-based resins [48], polyurethane foams [49,50] and some cation exchange resins [51]. Similarly to solvent extraction, there seem to exist several suitable systems for the recovery of rhodium in its cationic form in the presence of other precious and base metals, but only in non-chloride solutions and therefore these are not applicable to precious metals refining solutions.

Recently a newer class of separation reagents, which resemble IX resins, have been developed specifically for rhodium recovery. The technique is based on molecules which resemble crown ethers and are described as molecular recognition ligands [52]. The functional molecule, which is bound to a solid silica support, is designed and synthesized in order to selectively bind a specific metal species by carefully considering its geometry, size, charge and coordination affinity. A resin-like material called Superlig® 1 [53], able to separate Rh(III) and Ir(III) from the other PGM and some base metals from chloride solutions has recently been described. The species extracted are the hexachloroiridium and rhodium complexes, and therefore this material is believed to be most applicable when separating rhodium and iridium from highly concentrated chloride solutions, since it is only in these solutions that the hexachloro complexes are predominant, as discussed earlier (Figures 2.1 and 2.2). The exact extraction conditions have not been revealed except to say that solutions higher than 4M chloride are best (to help ensure $RhCl_6^{3-}$) and solutions as low as 1 ppm Rh/Ir can be treated. Also, the proton concentration of the solution is not problematic and a wide range of acidities can be treated.

SuperLig® 1 offers very good selectivity for rhodium and iridium over base metals and this makes possible its unique (to date) application at the head of the PGM flowsheet rather than at the end. Minor drawbacks seem to be that some platinum and palladium will be coextracted along with rhodium and iridium (separation factor about 75:1), and that the rhodium and iridium are usually eluted together, and must then be separated by some other method. Its major drawback, however, lies in the complex elution scheme which is required to completely strip the rhodium and iridium from the co-extracted platinum and palladium. Depending on whether the rhodium and iridium are eluted separately or concurrently, the eluent solutions are ethylenediamine at pH 1 and ethylenediamine at pH 10 with the simultaneous application of heat at a highly controlled temperature profile. Also, as the support material is not resistant to strong bases (pH>11) , the pH 10 elution stage must be well monitored to make sure that the alkalinity never rises to pH 11. It has been reported that three precious metals refineries may be proceeding with installation of a SuperLig® circuit for rhodium recovery [23,54], however, it has not been revealed whether any of the major producers are involved.

2.5 RHODIUM - TIN COMPLEXES

2.5.1 Rhodium-Tin Complexes in Aqueous Solutions

Analytical chemists have long made use of the rapid interaction between Rh(III) and Sn(II) for the trace determination of rhodium either by preconcentration through solvent extraction or by colorimetry. Because the chloro-complexes of rhodium often contain aquo ligands and are not easily extracted, the much more labile and non-aquated complexes, which are formed when rhodium complexes are allowed to react with $SnCl_2$ in acidic chloride solutions, have proven to be quite useful. In this work, the solvent extraction systems developed make use of Sn(II) to render rhodium extractable. It is necessary, therefore, to understand the interaction between rhodium and Sn(II).

A number of studies have been undertaken to identify and characterize the Rh-Sn complexes which are formed upon reaction [49,55]. Similarly to the case of pure rhodium chloride solutions, many different complexes can be formed. The interaction between Rh(III) and Sn(II) involves the replacement of the Cl^- and H_2O ligands of the initial rhodium complexes by $SnCl_3^-$ ligands as follows:

$$[RhCl_6]^{3-} + SnCl_3^- \rightarrow [RhCl_5(SnCl_3)]^{3-} + Cl^- \qquad (2.9)$$

$$[RhCl(SnCl_3)_5]^{3-} + SnCl_3^- \rightarrow [Rh(SnCl_3)_6]^{3-} + Cl^- \qquad (2.10)$$

$$\cdots$$

$$[Rh(SnCl_3)_6]^{3-} \rightarrow [Rh(SnCl_3)_5]^{4-} + SnCl_3^+ \qquad (2.11)$$

In the last reaction, the reduction of Rh(III) to Rh(I) occurs and is accompanied by the oxidation of Sn(II) to Sn(IV). It has been reported that this oxidation/reduction reaction occurs only after all chloride ligands have been replaced by $SnCl_3^-$ ligands [55], i.e., only from $[Rh(SnCl_3)_6]^{3-}$. The oxidation/reduction reaction is also believed to occur intramolecularly, that is, with one of the $SnCl_3^-$ ligands and not with free

Sn(II) complexes in solution.

The various complexes described in equations 2.9 to 2.11 have been separated and precipitated with tetramethylammonium chloride [56]. Typical Rh-Sn solutions are red, although it is reported that in some cases, yellow solutions can also be obtained. Interestingly, in addition to the above complexes, another complex was obtained from the yellow solution, but it was not described in great detail, except for its possible composition, $[RhSn_5Cl_{15}]^{3-}$. This complex was found to retain its yellow colour when dissolved in concentrated HCl acid (>3M) but to produce the usual red solutions when dissolved in < 3M HCl solutions. Given some of the subsequent work which has been carried out on Rh-Sn complex characterization, it is likely that the species precipitated was the protonated complex, $[RhH(SnCl_3)_5]^{3-}$.

The stability and abundance of the various Rh-Sn complexes depends on both the Sn:Rh ratio and on the presence of air. For example, at high Sn:Rh ratios, Rh(III) complexes are converted to Rh(I) complexes. Upon extended exposure to air, however, the Rh(I) complex slowly converts back to one or many unidentified Rh(III) complex(es) [55], one of which is most probably $[RhCl(SnCl_3)_5]^{3-}$. Because Sn(II) is susceptible to oxidation by air, if the Rh-Sn solution is exposed sufficiently long, the complexes will break apart to reform Rh-Cl and Sn(IV) complexes. At low Sn:Rh ratios (<6) no reduction of Rh(III) to Rh(I) occurs and many different Rh-Sn-Cl complexes may be present at the same time.

Through an extensive ^{119}Sn NMR study of the complexes formed by allowing $RhCl_3 3H_20$ to react with $SnCl_2$ (Sn:Rh molar ratio 7:1 or less) in 3M HCl, the ^{119}Sn NMR signal of each of the complexes in solution was determined [55]. Through this method, a speciation diagram for the various Rh-Sn complexes present in a 3M HCl solution at 25°C as a function of the Sn:Rh complex ratio was constructed. It is reproduced in Figure 2.5.

It is interesting to note that when the Sn:Rh solution molar ratio is six or less, it has been found that there is no free Sn(II) in solution [55]. Only when the ratio exceeds 6:1 does free Sn(II) become detectable. This means that all of the Sn(II) which is added to the rhodium solution is immediately used either as a ligand or to reduce Rh(III) to Rh(I).

The mixed Rh-Sn complexes are thought to be more labile than the chloride complexes of rhodium due to the strong π-acid nature of the $SnCl_3^-$ ligand [55] and therefore the replacement of $SnCl_3^-$ by another ligand is not subject to the same kinetic difficulties as is the replacement of chloride as a ligand. This may help to explain the tremendously improved response of such complexes to solvent extraction as opposed to the Rh-Cl complexes. These complexes are more labile than the Rh(III) chloride complexes and therefore may react much more readily with various organic extractants. In addition, the Rh-Sn-Cl complexes are not aquated (and may also be less hydrated) so they are not as hydrophillic as the mixed aquo-chloro complexes of Rh(III). Finally, it is also apparent that $[Rh(SnCl_3)_5]^{4-}$ is larger than the Rh(III) aquo-chloro complexes and therefore it might be easier to surround this species with the organic molecules, in the case of ion-pairing, than it is the smaller Rh(III)-Cl-H_2O complexes.

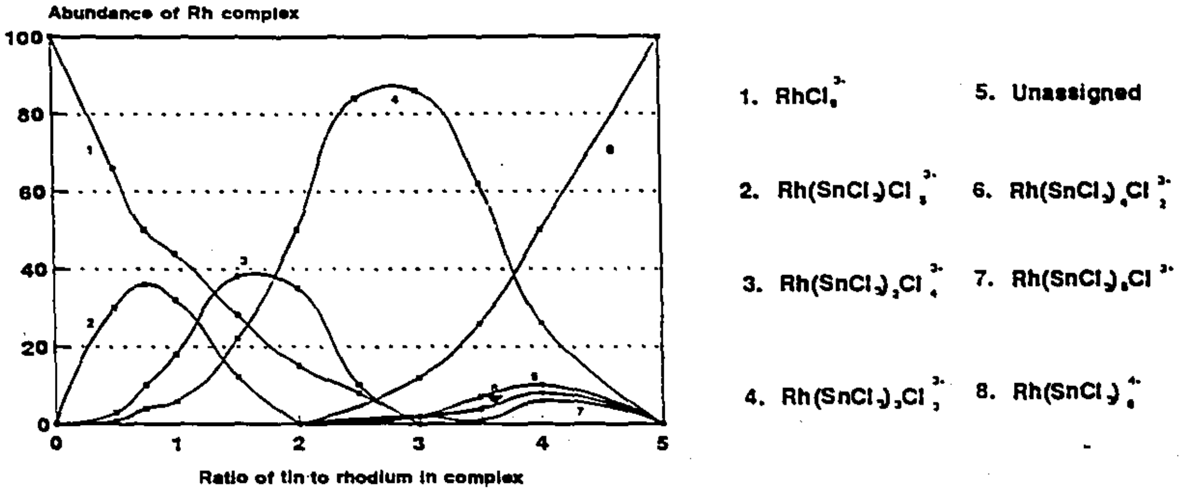

Figure 2.5: Rhodium-tin complexes speciation diagram in 3M HCl as per Moriyama et al.[58]

2.5.2 Rhodium-Tin Complexes in Organic Solutions

Some studies have characterized the Rh-Sn complexes extracted into organic solutions via ^{119}Sn NMR. One such study [57] involved the extraction of rhodium, in the presence of $SnCl_2$ at about 6:1 Sn:Rh molar ratio, from 2M HCl solutions using MIBK under an inert atmosphere. The complex extracted was characterized to be a rhodium hydride, $[RhH(SnCl_3)_4Cl]^{3-}$. This complex was not detected in the aqueous solution either prior to or after extraction nor has it been reported to exist in any other solution. It was reported that the feed solution containing $[Rh(SnCl_3)_5]^{4-}$ was red while the organic complex was yellow. The authors suggest that $[Rh(SnCl_3)_5]^{4-}$ is extracted and immediately undergoes oxidative addition of HCl with the simultaneous loss of one $SnCl_3^-$ ligand. The extracted complex was found to be unstable in air and to rapidly decompose to $[RhCl_3(SnCl_3)_3]^{3-}$ and another unidentified rhodium complex, of unknown oxidation state.

The formation/existence of the hydride complex identified here seem to be speculative since different conditions must be met for complex identification through ^{119}Sn NMR. One of these is satellite peak intensity (based on the natural abundance of ^{117}Sn versus ^{119}Sn isotopes) versus the main peak intensity. The ratio found here does suggest that the rhodium complex has four $SnCl_3^-$ ligands, but high level of noise in the baseline would make it difficult to accurately determine this ratio. Another condition which maybe used for Rh-Sn complexes is $^2J(^{103}Rh-^{119}Sn)$. Here the J value is far from the expected one and it seems to indicate that the complex is not a Rh(III) complex, as it would have to be if it were indeed a hydride. In appears to still be a Rh(I) complex and therefore, direct HCl protonation of $[Rh^I(SnCl_3)_5]^{4-}$ to $[Rh^IH(SnCl_3)_4Cl]^{3-}$ may prove to be more accurate. It should be pointed out here that a similar complex was found to exist in solutions after the dehydrogenation of propan-2-ol with Rh-Sn complexes [58]. The complex in that study was not identified except to give the ^{119}Sn NMR characteristics (which correspond perfectly with those of the above study). Again, whether the complex is truly a hydride or only a protonated species is difficult to say.

Another study [59] of Rh-Sn complexes in organic solutions has also revealed the presence of a hydride complex, $[Rh^IH(SnCl_3)_5]^{3-}$, in addition to the usual $[Rh^{III}Cl_{6-x}(SnCl_3)_x]^{3-}$ (where $2 \leq x \leq 4$) complexes [58]. Rh-Sn complexes are used as catalysts for the dehydrogenation of propan-2-ol to yield acetone and hydrogen gas. The hydride was found to exist only after the dehydrogenation process and was not detected in solution prior to this reaction. There is strong evidence to suggest that the complex which was proposed is in fact valid and it therefore appears that hydride complexes of Rh(III) may be formed.

More recently, a study on the complex extracted from HCl solutions with a quaternary ammonium chloride salt (AQ-336) in chloroform also identified a H-Sn-Rh complex [60]. It this case, the authors have found that $[Rh(SnCl_3)_5]^{4-}$ exists in the organic phase when the feed solution matrix is 0.5M HCl. However, if a strong acid is contacted with the loaded organic, then the extracted complex changes to $[RhH(SnCl_3)_5]^{3-}$ and this was attributed to the easy protonation of $[Rh(SnCl_3)_5]^{4-}$. The authors were also able to identify the $[RhH(SnCl_3)_5]^{3-}$ complex in the aqueous solutions when the acidity was greater than 3M HCl. Moriyama et al [55], who studied the aqueous complexes of rhodium in 3M HCl did not identify such a complex. The authors here do not refer to the H-Rh-Sn complex as a hydride. The simple, reversible, protonation reaction

$$\overline{[Rh(SnCl_3)_5]^{4-}} + \overline{H^+} - \overline{[RhH(SnCl_3)_5]^{3-}} \qquad (2.12)$$

(where overbars refer to species in the organic phase)

was proposed, suggesting that the complex is still a Rh(I) species. The authors also noted that the complex changed colour from the usual red to yellow upon protonation. Reaction 2.12 can be rewritten more rigorously, as follows,

$$\overline{[Rh(SnCl_3)_5\cdot(NR_4)_4]} + \overline{NR_4Cl\cdot HCl} - \overline{[RhH(SnCl_3)_5\cdot(NR_4)_3]} + 2\overline{NR_4Cl} \qquad (2.13)$$

2.5.3 Extraction of Rhodium-Tin Complexes

One of the groups which has done a considerable amount of work on the characterization of Rh-Sn aqueous solutions and extracted complexes, has also worked on the extraction Rh-Sn complexes through sorption by polyurethane foams [50]. This process is relatively similar to solvent extraction as it involves the separation/purification of a metal species via a transfer reaction to a different phase. The researchers found that rhodium in pure HCl solutions cannot be sorbed but that when $SnCl_2$ is allowed to interact with rhodium, then high distribution ratios can be obtained for rhodium.

It was determined that tin is co-extracted with rhodium and it is highly likely that it is extracted as part of a Rh-Sn complex since free Sn(II) complexes cannot be sorbed by polyurethane from similar HCl feeds. The Sn:Rh ratio in the extracted complex varies from 3.6 to 4.5 as the feed Sn:Rh ratio is increased from 3:1 to 20:1, respectively. The extraction degree was found to decrease with increasing temperature of the solution. No satisfactory explanation is given for this behaviour. Increased acidity helped to increase the amount of extracted rhodium due, most likely, to an increase in the number of polyurethane "active" sites. A description on the "active" sites was not provided, however, it seems reasonable to expect these to be the nitrogen atom and its lone pair of electrons.

An interesting effect of increased acidity is that it caused the amount of co-extracted Sn(II) to decrease. For a feed molar ratio of 10:1 Sn:Rh, the amount of co-extracted tin decreased from about 5 to 3.5 with an increase in acidity from 0.5M to 5M HCl [50]. The explanation provided by the authors has to do with the mass effect of the chloride ion in HCl and with the speciation of Sn(II)-chloride complexes. This does not seem reasonable since the only two expected complexes at 10:1 Sn:Rh ratio in such HCl solutions would be $[Rh(SnCl_3)_5]^{4-}$ and $[RhH(SnCl_3)_5]^{3-}$, both of which maintain the ratio 5:1 Sn:Rh. If the complex $[RhH(SnCl_3)_4Cl]^{3-}$ exists, however, then the ratio 3.5:1 could be more easily accepted.

The effect of the Sn:Rh ratio in solution was also studied and it was found that a dramatic increase in loading capacity occurs as the Sn:Rh ratio is increased from 3:1 to 6:1 [50]. This corresponds to the conversion of the $[RhCl_{6-x}(SnCl_3)_x]^{3-}$ complexes to $[Rh(SnCl_3)_5]^{4-}$. The loading capacity was found to continue to increase gradually up to 200:1 Sn:Rh (the maximum value tested).

The use of Sn(II) to enhance rhodium extraction was also tested for the extractant dihexyl sulfide (R_2S) [61]. This extractant can only extract small amounts of rhodium from HCl solutions (1 to 10% extraction from 1 to 8M HCl solutions, respectively), however, when Sn(II) is added, at Sn:Rh molar ratio 1:1, quantitative extraction occurs (from 4 to 6M HCl). At lower acidities, quantitative extraction can also be achieved if the tin concentration is increased. Although tin cannot be extracted when it is present as free Sn(II) chloride, tin is co-extracted along with rhodium. The extracted complexes were estimated to be $H_3[RhCl_5(SnCl_3)]\cdot 2R_2S$ and $H_3[RhCl_4(SnCl_3)_2]\cdot 2R_2S$.

The fact that quantitative extraction can be achieved at Sn:Rh 1:1 from 4-6M HCl solutions might be a little bit surprising in terms of the Rh-Sn speciation diagram shown in Figure 2.6. At 1:1, only about half of the complexes are Rh-Sn while the rest is still a mixture of aquo-chloro complexes. It is true, however that Figure 2.5 was constructed for 3M HCl and the speciation might change somewhat at higher acidities and chloride concentrations. Reaction 2.9, however would seem to indicate that the higher the chloride concentration, the lower the abundance of Rh-Sn complexes, which seem to be the opposite of what has been found in this study with the need for greater than 1:1 Sn:Rh at lower HCl concentrations and only 1:1 at higher HCl concentrations.

Stripping was attempted with 1M HCl but no rhodium could be stripped. Some tin could be stripped with this solution but multiple contacts are required and high temperatures (98°C) are necessary. When 0.4M thiourea was added to 1M HCl, however, both rhodium and tin could be stripped. At 25°C, 60% rhodium and 85% Sn could be stripped (CT=24 hrs) whereas at 98°C, quantitative rhodium and tin stripping was achieved in a single contact (CT=2 hrs).

Patents have also been issued to Japanese researchers [62] who identified a tin-based solvent extraction process for rhodium. The extractant is, once again, di-n-hexylsulfide. A Sn:Rh molar ratio of about 10-12:1 is suggested for best results for solutions ranging in acidity from 0.5 to 12M HCl. Quantitative rhodium extraction can be obtained under these conditions. The co-extracted tin is scrubbed with 0.5M HCl and then the rhodium can be directly recovered from the organic by precipitation of a rhodium sulfide with either $H_2S_{(g)}$ or Na_2S.

2.6 RHODIUM IN SULFATE AND SULFITE SOLUTIONS

For the solvent extraction systems developed here, the stripping solutions were either sulfuric acid or a mixture of sodium sulfite in hydrochloric acid. The speciation of rhodium in sulfate and sulfite solutions would therefore have been useful, but, very few studies have been performed on the interactions of Rh(III)/Rh(I) with either of these anions (SO_4^{2-} or SO_3^{2-}).

2.6.1 Rhodium in Sulfate Solutions

In the case of sulfate solutions, complexes such as $[Rh_2(SO_4)_3]^\circ$, and $[Rh(SO_4)_2]^-$ [63], as well as $M^I_3Rh(SO_4)_3$ and $M^IRh(SO_4)_2$ salts (where M is a monovalent cation) [64] have been identified. One study on the nature of Rh-Sn-SO_4 complexes, which could be of particular interest here, has characterized complexes such as $[RhSn_5(SO_4)_7]^-$ and $[RhSn_5(SO_4)_9]^{5-}$ [65] (with Rh once again in the III state). The aqueous medium for this study, however, was basic solutions of sodium hydroxide, and no similar study in an acidic medium was found.

The studies which have been performed usually start with the dissolution of $Rh(OH)_3$ in H_2SO_4 to obtain, first, $[Rh(H_2O)_6]^{3+}$ and then, depending on the temperature, acidity and sulfate concentration, a number of mixed complexes are formed. These include mixed aquo-hydroxy rhodium complexes, mixed aquo-hydroxy-sulfate complexes and oxy-sulfate-bisulfate rhodium complexes [66]. A whole spectrum of anionic, neutral and cationic complexes may therefore be present in rhodium sulfate solutions. Clearly, much remains to be learned about the interactions of Rh(III)-SO_4^{2-} and Rh(III)-Sn(II)-SO_4^{2-}, and more investigations must be performed before a better defined speciation of the complexes in solution can be presented.

2.6.2 Rhodium in Sulfite Solutions

In the case of sulfite, it is known [67] that the SO_3^{2-} group may act either as a mono- or bi-dentate ligand, forming chelates or bridged complexes, through either the oxygen of sulfur atoms. Infra-red spectra can often be used to differentiate between all of these different possibilities. A number of rhodium complexes containing one or more sulfite group (SO_3^{2-}) have been reported; $[Rh(NH_3)_4(SO_3)(CN)]$, for example, is reported to be S-bonded monodentate [68] while $K_3[Rh(SO_3)_3]$ is bi-dentate [69]. Unfortunately, there does not appear to be any study of rhodium chloride solutions in the presence of sulfite. There are sufficient studies [67-69], however, to expect that rhodium-sulfite complexes do exist.

Because in one of the solvent extraction systems described in this work, sodium sulfite, dissolved in HCl solutions, is used as a strip medium, the sulfite species existing in solution should be known. There is some controversy over the existence of H_2SO_3 in solution, but it is now generally accepted that this species does not exist in aqueous solutions [70]. According to Cotton and Wilkinson [4], the equilibria in aqueous solutions of SO_2 are best represented by:

$$SO_{2\,(g)} + xH_2O \rightarrow SO_2{\cdot}xH_2O \ \text{(hydrated } SO_2\text{)} \qquad (2.14)$$

$$[SO_2{\cdot}\,H_2O \rightarrow H_2SO_3 \quad K <\!<\!< 1] \qquad (2.15)$$

$$SO_2{\cdot}xH_2O \rightarrow HSO_3^- + H_3O^+ + (x\text{-}2)\,H_2O \qquad (2.16)$$

$$HSO_3^- \rightarrow SO_3^{2-} + H^+ \qquad (2.17)$$

Figure 2.6 shows the Pourbaix diagram for the SO_2 - H_2O system [71].

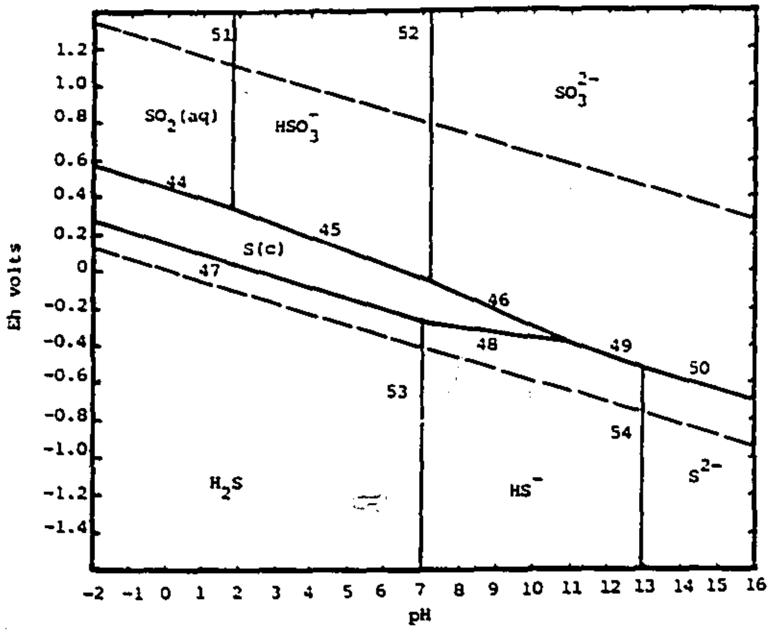

Figure 2.6: Pourbaix diagram for the SO_2-H_2O system, taken from [71].

It is known that solutions of SO_2 can be oxidized by air, however this reaction is very pH dependant and it has been reported that under acidic conditions, the oxidation would be much slower than in neutral solutions. It has also been reported that the presence of organics in many cases also inhibits the oxidation reaction [70].

2.7 KELEX 100 AND RELATED EXTRACTANTS

Both of the solvent extraction systems developed in this work make use of Kelex 100 as extractant. It is worthwhile, then, to briefly review some of the most important characteristics of this extractant.

The structure of Kelex 100, a 7-substituted derivative of 8-hydroxyquinoline, is shown in Figure 2.7 [72]. The purity of the as-received product has been determined to be about 82% [73], with an additional 5% of the material being other quinoline-based complexing agents. In this work the extractant was subjected to an acid-wash prior to its use to remove acid soluble impurities. Such a precaution has been reported to help increase the purity of the organic [74].

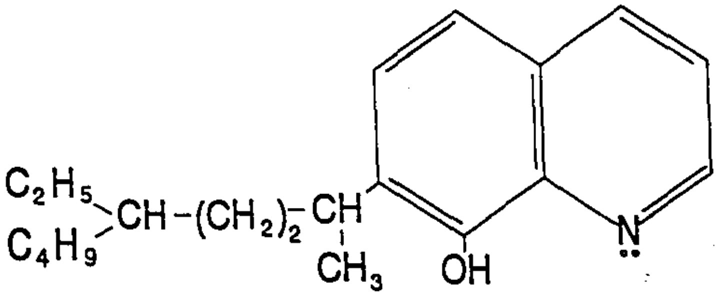

Figure 2.7: Structure of the active component of Kelex 100, taken from [72].

A most interesting feature of Kelex 100 is that it can extract via two different mechanisms. One of these is through chelation, via the loss of the proton of the hydroxyl group and the direct bond between O^- and a metal cation. The lone pair of electrons on the nitrogen atom then serves to form a coordination bond and stabilize the chelate structure. An example of chelation is the extraction of Pd(II) from chloride solutions as shown in the following equation [33]:

$$PdCl_4^{2-} + \overline{2HQ} \rightarrow \overline{PdQ_2} + 4Cl^- + 2H^+ \tag{2.18}$$

(where HQ refers to Kelex 100, taken from hydroxyquinoline)

The second possible extraction mechanism is ion-pair formation. In this instance, the nitrogen atom becomes protonated via its basic lone pair of electrons and, for charge neutrality, a corresponding anion is also associated. The extractant can then behave as an anion exchanger, releasing the anion associated to the protonated nitrogen and simultaneously extracting an anionic metal species. This is the mechanism of extraction for Pt(IV) from chloride solutions as shown in the following equations [34]:

$$\overline{HQ} + HCl - \overline{H_2Q^+Cl^-} \qquad (2.19)$$

$$PtCl_6^{2-} + \overline{2H_2Q^+Cl^-} - \overline{[PtCl_6^{2-}\cdot(H_2Q^+)_2]} + 2Cl^- \qquad (2.20)$$

For ion-pair formation, it is important that the aqueous solution be of relatively high acidity in order for reaction 2.21 to proceed. The extraction of HCl by Kelex 100 has been studied recently [75] and the concentration of HCl in the organic as a function of the HCl in the aqueous solution has been determined. Figure 2.8 shows a reproduction of these results.

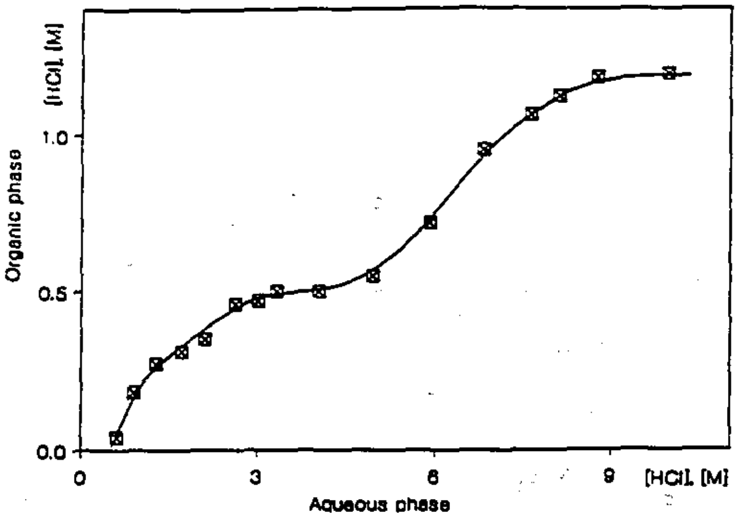

Figure 2.8: Extraction of HCl by 0.55M Kelex 100, taken from Kyuchoukov and Kounev [75].

From Figure 2.8, it can be seen that the 0.55M extractant is fully protonated at 3M HCl. A second protonation occurs beyond acidities of 5M HCl. This can be due either to the uptake of a second HCl molecule, as suggested by the authors [75], or by the formation of microemulsions and the simultaneous solubilization of more acid in the organic phase [20]. The exact acidity necessary to achieve full protonation is not clearly defined and most probably also depends on the alcohol content of the organic. Another recent study on the extraction of acid by extractants very similar to Kelex 100, TN reagents, also 7-substituted derivatives of 8-hydroxyquinoline, and containing three times the molar concentration of alcohol (tridecanol) showed that the organic is fully protonated at acidities of 2M HCl [76]. Further acid uptake was also found to occur beyond 5M HCl, but was believed to be due to the protonation of the alcohol modifier.

A study of the organic phase composed of Kelex 100 (0.15M) , tridecanol (0.20M) and kerosene, after contact with aqueous HCl solutions was recently performed [34]. It was determined that a significant amount of water is solubilized in the organic phase. For example, with a 4M HCl feed, the organic was found to contain four water molecules per Kelex 100 molecule. The presence of microemulsions in the organic phase was proposed and through viscosity and light-scattering measurements, it was shown that microemulsions begin to form to a significant extent beyond 1.5M HCl and that their size is about 10 nm [20]. The effect of the alcohol concentration on water uptake was also examined. It was determined that the amount of solubilized water decreased with increasing alcohol content for a given acidity (1.4M HCl). It is believed that at sufficiently high concentrations of alcohol, strong interactions in the microemulsions dominate and lower the amount of water which is extracted.

Kelex 100, and related 7-substituted derivatives of 8-hydroxyquinoline, have been studied for the extraction of a number of elements, from a wide range of aqueous media. Kelex 100 was originally developed for copper extraction from weakly acidic sulfate media [77], through chelation. Problems encountered with selectivity and acid extraction during the acidic stripping stage, however prevented the commercial application of such a process. A recent study focused also on the extraction of copper, but this time for the transfer of copper from acidic chloride solutions, through ion-pair formation, to dilute sulfate solutions [75]. Although this is not believed to be an industrial process at the present time, it does show the continued interest in this versatile extractant.

Kelex 100 has been adopted as the preferred extractant for gallium recovery from alkaline aluminate solutions and this process has been patented and is being used in France [78] by Rhone-Poulenc. Other metals also investigated include Ge(IV), Co(II), Cd(II), Zn(II), Ni(II) and Pb(II) [79, 80]. The extraction of some of the precious group metals (Au(II), Pt(IV), and Pd(II)) have also been investigated from HCl solutions [33,34,81].

Clearly then Kelex 100 has attracted significant attention as potential extractant for a wide variety of elements, in aqueous media ranging from the alkaline region, passing through the weakly acidic region, and to the strongly acidic one. The investigation of its possible use as extractant for rhodium from acidic chloride media should therefore not be surprising.

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CHAPTER 3
EXPERIMENTAL

3.1 REAGENTS

3.1.1 Organic Solutions

The organic extractant used in the course of this investigation was Kelex 100[1] (lot 3349-72, kindly supplied by Sherex Chemical Co., now WITCO Co., Ohio, USA), a 7-substituted derivative of 8-hydroxyquinoline. The chemical structure has already been presented in Figure 2.7. Kelex 100 is reported to have a saturated side chain of eleven carbon atoms, having moderate steric hindrance, an average molecular weight of 299 g/mol, as well as an "as received" purity of 82%, with an additional 5% content described as quinoline-based impurities [1,2].

Prior to its use, the extractant was diluted with Solvesso 150[2] (a diluent with 97% aromatic content), and tridecanol (Harcros Chemicals) was added as phase modifier. The relative percent composition of the organic solution was varied in some cases, but the usual composition was 2 vol.% Kelex 100 (0.058M, based on total quinoline content), 10 vol. % tridecanol (0.41M) in Solvesso 150. The organic solutions were not used directly as prepared, but were first submitted to a conditioning stage. This involved contacting the organic with an equal volume of 3M HCl for three minutes to wash out all acid soluble organic components. The acidified organic phase was then subjected to three consecutive three-minute deionized water contacts also at an aqueous to organic (A/O) ratio of one. In general, one litre batches of organic solution were prepared and stocked for further

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[1] Proprietary product of WITCO Co (previously Sherex Co.).

[2] Proprietary product of Exxon Chemicals Co.

use.

3.1.2 Aqueous Solutions

The aqueous solutions were prepared from water deionized in a two-column Cole Parmer ion exchange system. Rhodium solutions were prepared using $Na_3RhCl_6 \cdot H_2O$ (Aldrich Chemicals), or $RhCl_3$, (Sigma Chemicals). Other reagents, such as $SnCl_2$ and acids, were of reagent grade. All of the aqueous solutions were prepared fresh, immediately before use, except for the sulfuric acid strip solution of the system described in Chapter 4 which was prepared as two litres stock.

The standard feed medium for the system described in Chapter 4 was 1.5M HCl + 0.75M $MgCl_2$ while that of the system described in Chapter 5 was 1.5M HCl +1.5M $MgCl_2$. The standard strip medium for the system described in Chapter 4 was 1.7M H_2SO_4 + 1M Na_2SO_4, while that of the system described in Chapter 5 was 0.5M Na_2SO_3 in 2.4M HCl.

3.2 EXPERIMENTAL METHODOLOGY

3.2.1 Rhodium Feed Pretreatment with $SnCl_2$ (Activation Stage)

The feed solutions were prepared by dissolving appropriate amounts of a rhodium salt in a $HCl/MgCl_2/H_2O$ solution. The rhodium concentration was typically in the order of 4×10^{-3}M (400 ppm). This solution was then heated to 70°C at which point the required amount of $SnCl_2$ was added. The Rh-Sn solution was then maintained at 70°C for fifteen minutes. A gradual colour change from red-pink, to orange, to dark wine-red (when >6:1 Sn:Rh was used) was observed. The "activated" solution was then removed from the heat and allowed to cool to room temperature (typically 30 minutes) prior to contact with the organic phase.

3.2.2 Procedure for Equilibrium Tests

Most of the tests were performed using 125 mL separatory funnels fixed to a Burrell automatic wrist action shaker (model 75). Prior to contact, a sample of the activated feed solution was taken for subsequent rhodium and tin analysis. For the extraction stage, the aqueous and organic solutions were usually mixed at a phase volume ratio of one during five minutes. Due to the substantial value of rhodium, the volume of solution was often kept to a minimum and, for many tests, only 15 to 25 mL of each phase was used. After phase separation, about five to fifteen seconds, samples of the raffinate were kept for analysis. In some cases, a sample of the organic phase was also retained for analysis for mass balance verification. Stripping was also usually performed at an aqueous to organic ratio of one and the contact time was set at fifteen minutes for the system described in Chapter 4, and at twenty minutes for the system described in Chapter 5. Samples of each strip solution were kept for analysis.

In some cases, the extraction and stripping stages were performed in mechanically agitated reaction vessels for potential measurements, temperature control or to perform these stages under a nitrogen atmosphere. In these instances, mixing was achieved using a three-blade impeller. Unless otherwise stated, the equilibrium tests were performed at room temperature, 23±2°C.

3.2.3 Procedure for Kinetic Tests

A kinetic investigation of the stripping stage for the low Sn:Rh (3:1) system described in Chapter 5 was performed. A special experimental set-up was required and a schematic diagram of the equipment is shown in Figure 3.1. In order to maintain constant the aqueous to organic interfacial area (A/O), an organic-permeable membrane was used to separate the two phases. The membrane, composed of polytetrafluoroethylene (PTFE), was purchased from W.L. Gore and Associates, Inc., Maryland, and it can be described as having 45μm pore size and 75,9 porosity. An eight centimetre diameter interfacial region was used and the interfacial area can therefore be calculated as 38.2 cm^2.

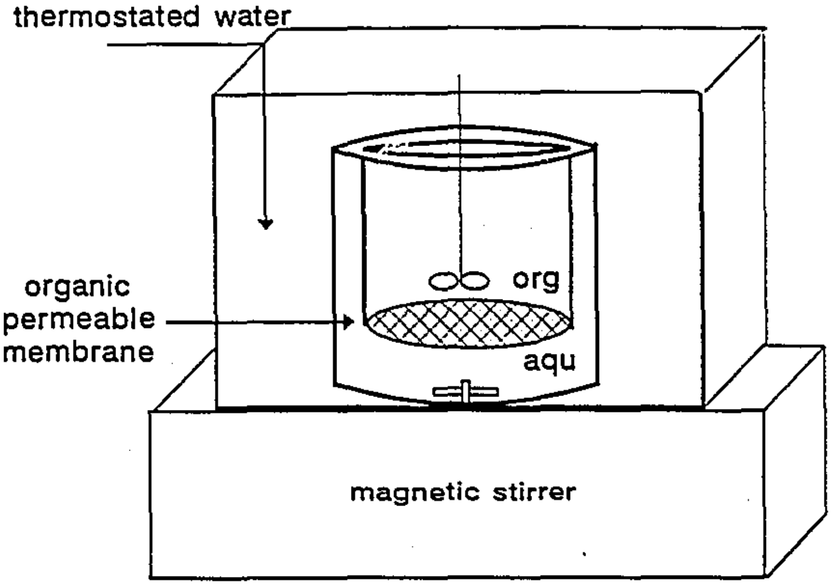


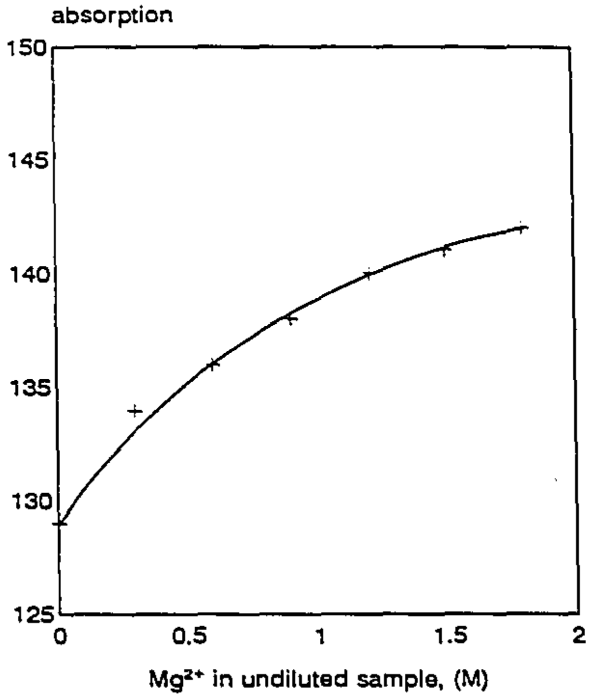
Figure 3.1: Experimental set-up for the kinetic investigation.

The aqueous strip solution (110 mL) was placed at the bottom of the flask and the membrane was then placed over it in such a manner as to be in complete contact with the aqueous solution. This ensured that the less dense, permeable organic would not be able to cross the membrane, enter the aqueous phase and change the overall interfacial area, but could only go as far as filling the membrane pores. A freshly prepared loaded organic (55 mL) was then placed over the membrane. Both solutions were stirred independently and small samples (0.5 - 1.0 mL) of the organic were removed at fixed intervals for metal content determination. Sampling was therefore possible without disturbing the system. The aqueous solution was stirred with a magnetic stirrer while the organic phase was stirred with a radial flow impeller. The temperature was fixed, usually at 25°C by immersing the reaction vessel in a thermostated water bath as depicted in Figure 3.1.

3.3 ANALYTICAL DETERMINATIONS

3.3.1 Metal Content

The metal concentrations were determined by atomic absorption using either a 357 Instrumentation Laboratory or a Perkin Elmer 3110 spectrometer. The aqueous samples and standards were diluted to the linear region using a mixture of HCl and H_2SO_4, such that matrix matching was possible. In addition, for both rhodium and tin, a nitrous oxide-acetylene flame was used rather than the more common air-acetylene flame, in order to minimize the effect of Na^+ and Mg^{2+}. Magnesium, especially, was found to be a harmful element for rhodium analysis as it causes significant positive deviation when present in high concentrations. Figure 3.2 shows the absorbance value for a fifteen ppm rhodium standard solution but containing increasing amounts of magnesium chloride. Up to 10% deviation can be seen in solutions containing 1.5M Mg^{2+}. Clearly, for the feed samples of Chapter 5, where 1.5M $MgCl_2$ was added, it was important to match the solution matrix, otherwise the rhodium content in the feed was over-estimated which caused the stripping degree to be calculated as lower than it actually was.



15 ppm Rh solution, nitrous oxide flame
samples diluted 20 times

Figure 3.2: Effect of Mg^{2+} on rhodium absorbance.

The organic samples were diluted with the usual organic solution. The rhodium organic standards were prepared by quantitatively extracting a solution of the aqueous rhodium standard previously activated with tin into a fresh organic and diluting to the linear region. The tin organic standards were calculated from the mass balance of the feed and raffinate.

In general, extraction was calculated as the difference in Rh concentration between the feed and the raffinate (no phase volume changes were found when measured).

$$\%\ \text{Extraction} = \frac{[\text{Rh in feed}] - [\text{Rh in raffinate}]}{[\text{Rh in feed}]} \times 100 \qquad (3.1)$$

Similar calculations were performed for stripping. As mentioned above, in some cases, the organic phases were also analyzed to ensure that good mass balance was obtained. A relative difference of less than 5% was found.

3.3.2 Other Analytical Measurements

Standard analytical titrations were used for such measurements as acidity and chloride ion concentration [3]. Titrations for Sn(II) concentrations were performed in hydrochloric acid media with ferric chloride under constant N_2(g) bubbling.

A number of other techniques/equipment was also used, such as FTIR, UV-visible, and Raman spectrometers (RTI 30 Dilor equippped with a Spectra-Physics 2000 Krypton ion laser; 647.1 nm radiation with a power of about 0.1W). No special techniques were used and therefore no further details will be given here.

^{119}Sn nuclear magnetic resonance (NMR) was also employed during the course of this work. The spectra were recorded at room temperature on two different spectrometers: a Bruker AC 300P spectrometer at 111.92 MHz and a Bruker AM 250 spectrometer at 93.27MHz. All chemical shifts are reported relative to an external $Sn(CH_3)_4$ reference. Single spectra of 100 000 Hz width were recorded. In all case, the NMR samples were stored under argon.

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CHAPTER 4

THE HIGH Sn:Rh ($\geq$ 6) SYSTEM

4.1 INTRODUCTION

The primary aim of this research was to develop an industrially interesting solvent extraction system for rhodium from chloride solutions. The bulk of the work therefore focused on process identification and development rather than on the fundamental reaction chemistry of each of the stages making up the system. Two different solvent extraction systems, using Kelex 100 as extractant, were developed during this work and they are described separately in Chapters 4 and 5. Both systems are based on an initial solution pretreatment step, the activation stage, which involves the reaction of the rhodium feed solution with $SnCl_2$. One of the main differences between the two systems is in the amount of tin required.

In this Chapter, a solvent extraction system making use of a Sn:Rh molar ratio of $\geq$6 :1, and which has been the subject of a US patent [1], is described. The system is composed of three main stages which are activation, extraction and stripping. It was quickly discovered that while both the activation and extraction stages are straightforward, the stripping stage can be quite problematic. Most of the work therefore focused on the stripping stage and consequently, some areas of the system were not studied in great detail because they were found, from a practical point of view, to be satisfactory.

To describe the system, a basic overview of the activation stage is given first. The equilibrium extraction results are then presented and the overall extraction reaction and mechanism are identified. Next, the effects of the most important parameters for the sulfuric acid stripping stage are discussed and the stripping reaction products are reported. A conceptual process flowsheet is presented at the end of this Chapter.

4.2 ACTIVATION

The first part of the solvent extraction system is the activation stage which involves the interaction of the rhodium feed solution with stannous chloride. As described in section 2.5.1, depending on the Sn:Rh ratio in solution, many different Rh-Sn complexes can co-exist. For the solvent extraction system described in this Chapter, solutions having a Sn:Rh molar ratio ≥ 6:1 respond best which implies that the activated complex, $[Rh(SnCl_3)_5]^{4-}$, is involved.

The activated feed solutions were briefly characterized, through ^{119}Sn NMR, to ensure that $[Rh(SnCl_3)_5]^{4-}$ is truly the complex that exists in solution. The spectrum of a 12:1 Sn:Rh solution (shown in Figure 4.1) was obtained and two distinct signals were found. One of these is a doublet at δ 4.2 ppm (J=811 Hz) with four satellite peaks. Based on a very similar signal, a doublet with four satellites, found by Moriyama et al. [2] at δ 5.1 ppm (J=806 Hz), the species giving rise to this signal was confirmed to be $[Rh^{I}(SnCl_3)_5]^{4-}$. The other signal found, a singlet at δ -444.3 ppm, can be attributed to the free Sn(II) chloride complexes in solution. The ^{119}Sn NMR spectrum for a $SnCl_2$ solution (in the same aqueous medium as the mixed Sn-Rh solution) showed a singlet at δ -413.5 ppm, as presented in Figure 4.2, but it is known that the location of the stannous chloride peak is highly dependant on its concentration [2,3]. For example, Moriyama et al. [2] found that the free Sn(II) peak shift from δ -371.1 ppm to δ -403.6 ppm as the Sn:Rh ratio is increased from 7:1 to 10:1.

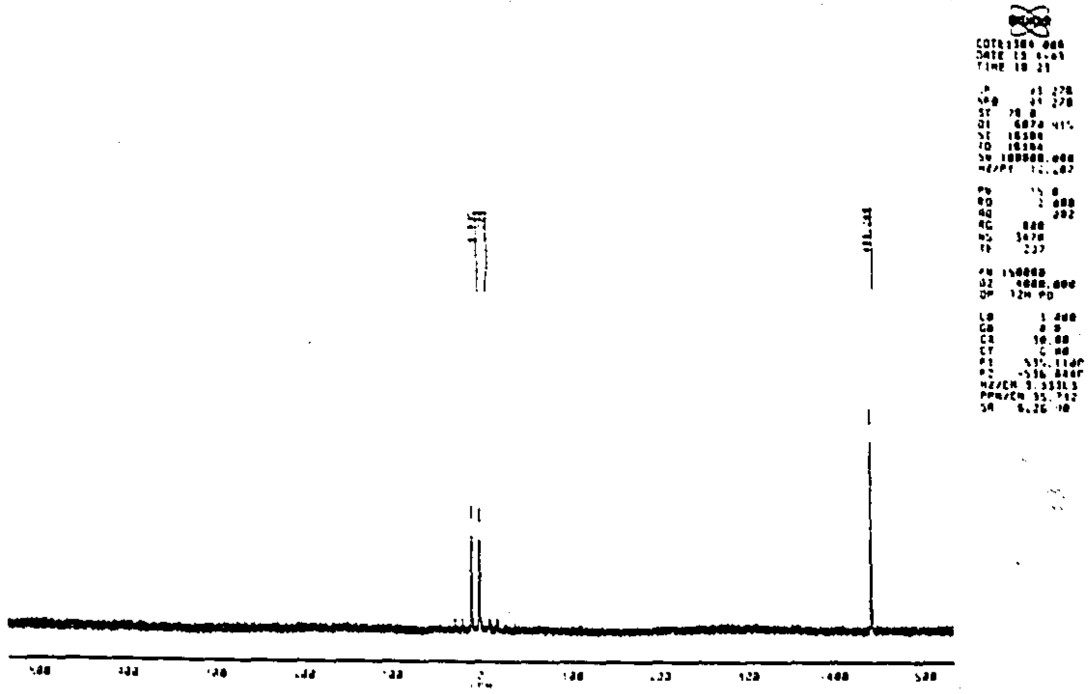


Figure 4.1: ^{119}Sn NMR spectrum of a 12:1 Sn(II):Rh solution (about 58mM Rh and 0.68M Sn) in 1.5M HCl+ 0.7M $MgCl_2$.

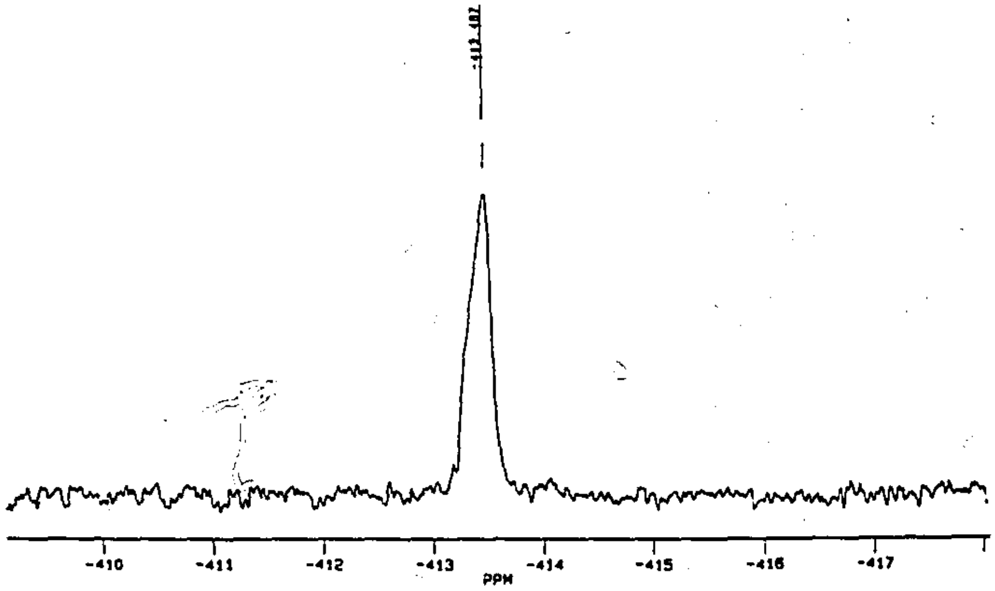


Figure 4.2: ^{119}Sn NMR spectrum of a 0.1M $SnCl_2$ solution in 1.5M HCl + 0.7M $MgCl_2$.

No other Rh-Sn complexes were detected through ^{119}Sn NMR in the activated feed solution.

In this work, activation was performed by heating the rhodium chloride feed solution, to which the desired quantity of $SnCl_2$ had been added, at 70°C for fifteen minutes. Rhodium feed solutions freshly prepared from Na_3RhCl_6 or stocked for well over a week showed no difference in response to activation. The activation reaction can be followed visually through a series of colour changes which start from the initial pink, $[RhCl_{6-x}(H_2O)_x]^{3-}$ complexes, transforming into bright orange, $[RhCl_{6-x}(SnCl_3)_x]^{3-}$ complexes, and finally achieving the characteristic dark wine-red colour of $[Rh(SnCl_3)_5]^{4-}$. Although such visual observations could be used as a rough guide to follow activation, a more reliable, yet quick and simple control, might be required in an industrial setting to ensure that activation is complete and that $[Rh(SnCl_3)_5]^{4-}$ has been obtained. One such method is through UV spectroscopy. It was found that for solutions of both $[RhCl_{6-x}(H_2O)_x]^{(3-x)-}$ and $[RhCl_{6-x}(SnCl_3)_x]^{3-}$ complexes, a band exists at about 250 nm, whereas this band cannot be observed in $[Rh(SnCl_3)_5]^{4-}$ solutions. The band has been attributed to the Rh-Cl bond [4,5]. Since the $[Rh(SnCl_3)_5]^{4-}$ complex has no direct Rh-Cl bond, the disappearance of a signal at 250 nm indicates the transformation of the $[RhCl_{6-x}(SnCl_3)_x]^{3-}$ complexes to the Rh(I) complex. The UV spectra of solutions having increasing Sn:Rh ratios are shown in Figure 4.3. Also included in Figure 4.3 are the spectra for pure Rh-Cl and $SnCl_2$ solutions. The spectrum for stannic chloride, $SnCl_4$, was found to be identical to that of stannous chloride, $SnCl_2$, with a singlet peak at 207 nm. In Figure 4.3, the increase in intensity of the band near 205 nm with increasing Sn:Rh ratio is simply due to the increase in total tin concentration.

The use of fifteen minutes heating time at 70°C for the formation of $[Rh(SnCl_3)_5]^{4-}$ is not mandatory, but rather it is simply a method of achieving the complex quickly. If for economic reasons it is preferred, in industry, not to heat the feed solution,

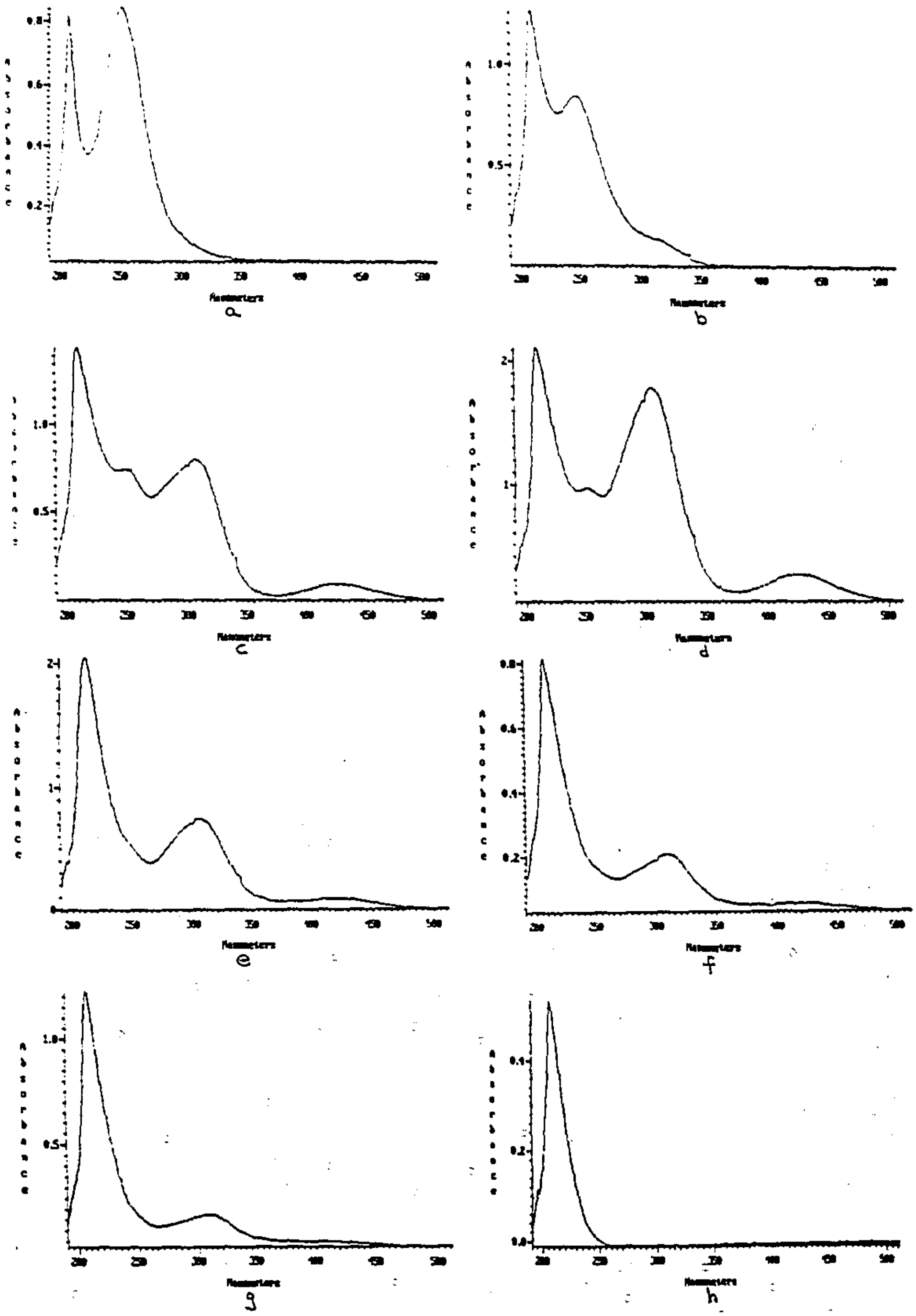


Figure 4.3: UV spectra of solutions having increasing Sn(II):Rh molar ratios; (a) Rh-Cl solution; (b) Sn:Rh 1:1; (c) Sn:Rh 3:1; (d) Sn:Rh 5:1; (e) Sn:Rh 9:1; (f) Sn:Rh 12:1; (g) Sn:Rh 20:1; (h) $SnCl_2$ solution.

then the mixed Rh-Sn solution can be left to stand at room temperature to achieve complete activation, i.e., the formation of $[Rh(SnCl_3)_5]^{4-}$.

UV spectroscopy was used to determine that at 25°C, for a 12:1 Sn:Rh solution containing 4×10^{-3}M Rh, three hours is sufficient to achieve complete activation. Spectra, not presented here, were recorded every half hour and showed the gradual reduction in the band at 250nm until its final disappearance after three hours. The reduction and disappearance in this band was accompanied by the ever increasing darkening of the solution to wine-red.

In the case where room temperature activation is preferred, care would have to be exercised in storing the feed solution since Sn(II) can be easily oxidized by air to Sn(IV) [6], eventually causing the $[Rh(SnCl_3)_5]^{4-}$ complex to break apart. For practical purposes, it was found, through ^{119}Sn NMR, that in a forty-eight hour old solution containing 4×10^{-3}M Rh and 0.05M Sn, $[Rh(SnCl_3)_5]^{4-}$ is still the only detectable rhodium complex in the solution (doublet at δ 3.0 ppm (J=818) and free Sn(II) signal at δ -432.8 ppm). If the solution is exposed for five days, however, then the UV spectrum shows that the $[Rh(SnCl_3)_5]^{4-}$ complex has transformed into $[RhCl_{6-x}(H_2O)_x]^{3-}$complexes, which are not quantitatively extractable. Stannous titration also revealed that all tin in solution had been oxidized to the stannic state. Depending on the concentration of tin in solution, then, there is only a definite period of time during which the activated solution can be used before it is no longer "activated".

Since Sn(II) can be easily oxidized by air, the oxidation rate of Sn(II) to Sn(IV) at 70°C by atmospheric oxygen was determined in order to ensure that sufficient Sn(II) would always be present for the experiments. An approximate rate of 6×10^{-3}M/hr was determined for a solution (4×10^{-3}M Rh, $4,8\times10^{-2}$M Sn(II), 1,5M H^+, 4M Cl^-) left to stand under atmosphere, without agitation, at 70°C, which for most experiments represents only about 8% loss of the tin in solution after fifteen minutes.

The activation stage can therefore be summarized through the following reaction:

$$RhCl_{6-x}(H_2O)_x^{(3-x)-} + ySnCl_3^- \rightarrow [Rh(SnCl_3)_5]^{4-} + (6-x)Cl^- + xH_2O + (y-6)SnCl_3^- + SnCl_3^+ \quad (4.1)$$

(where $0 \leq x \leq 6$ and $y \geq 6$).

The species written in equation 4.1 are not the most abundant in the aqueous solution used here (1.5M HCl + 0.75M $MgCl_2$) and equation 4.1 could be rewritten as:

$$RhCl_5(H_2O)^{2-} + ySnCl_4^{2-} \rightarrow [Rh(SnCl_3)_5]^{4-} + 8Cl^- + H_2O + (y-6)SnCl_4^{2-} + SnCl_6^{2-} \quad (4.2)$$

(where $y \geq 6$).

4.3 EXTRACTION

Once it was established that $[Rh(SnCl_3)_5]^{4-}$ is the only detectable rhodium complex in the activated solutions of ≥ 6:1 Sn:Rh, the extraction behaviour of this complex with Kelex 100 was studied through both equilibrium tests and chemical characterizations.

4.3.1 Equilibrium Studies

To determine, for all further tests, the time required to achieve equilibrium distribution of rhodium, an experiment measuring rhodium (and tin) extraction levels with contact time was performed and the results are presented in Figure 4.4. It was found that for a 1.4×10^{-2} M Rh solution having a 12:1 Sn:Rh ratio in 1.5M HCl, rhodium extraction was highest at short contact times, even as low as one minute, revealing that the rhodium extraction kinetics are extremely rapid. With increasing contact time, however, rhodium extraction decreased while that of free tin species increased. This indicates that the initially extracted $[Rh(SnCl_3)_5]^{4-}$ is slowly replaced in the organic phase for free Sn(II)-chloride complexes such as $SnCl_3^-$ and $SnCl_4^{2-}$. Extraction contact times of five minutes were chosen, for all further tests, as this allowed for maximum rhodium extraction, with no exchange of rhodium for free tin species under this condition.

The effect of contact time on Sn(II) extraction from pure stannous chloride solutions was also studied and, as expected, it was found that extraction increased with increasing contact time. However, in the case where there is no competition for the Kelex extractant, the extraction of tin reached a maximum sooner (ninety minutes) than in the mixed Rh-Sn solutions.

The exchange of an extracted species, by Kelex 100, with a different one is not new and this behaviour has been reported to occur in chloride solutions of Pt(IV) and Pd(II) [7]. The Pt(IV) complex, $PtCl_6^{2-}$, is rapidly extracted first, as an ion-pair, and is then exchanged for the more slowly extracted Pd(II) chelate in the organic phase. The replacement is simply due to the higher equilibrium extraction constant of a more slowly extracted complex over a faster extracted one.

Since the solvent extraction system is based on the addition of Sn(II) to render rhodium extractable, the amount of tin required to obtain quantitative extraction was determined (Figure 4.5). Also included in this Figure is a curve, based on Figure 2.5, showing the abundance of mixed Rh/Sn complexes at the various ratios. The experimental extraction results closely follow the abundance of Rh-Sn complexes with quantitative rhodium extraction occurring at a Sn:Rh molar ratio of about 2.8:1. This corresponds to the ratio at which there are no free Rh-Cl complexes in solution and all of the rhodium contains at least one $SnCl_3^-$ ligand [2]. Clearly then, it is possible to extract both the $[RhCl_{6-x}(SnCl_3)_x]^{3-}$ complexes and $[Rh(SnCl_3)_5]^{4-}$.

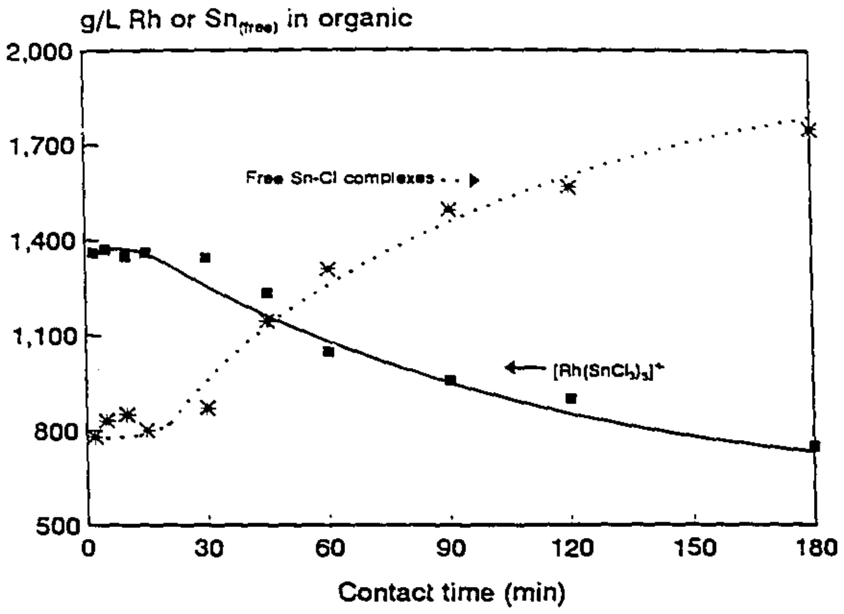


Figure 4.4: Extraction of Rh and free Sn(II) as a function of contact time.

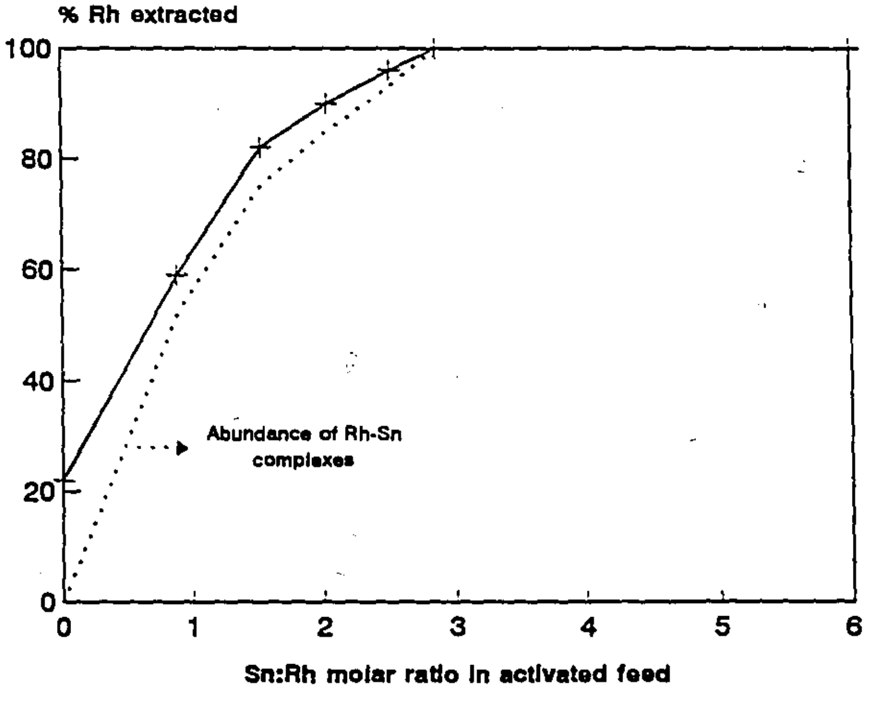


Figure 4.5: Effect of Sn(II):Rh ratio in feed solution on rhodium extraction (solid line). The abundance of Rh-Sn complexes (dashed line) is taken from the speciation diagram of Moriyama et al.[2].

The reasons for which the system is suitable mostly for $[Rh(SnCl_3)_5]^{4-}$ are addressed in the stripping section (4.4.3). Increasing the tin concentration to about 30:1 Sn:Rh molar ratio did not hinder the rhodium extraction (at CT=five minutes), which indicates that initially, $[Rh(SnCl_3)_5]^{4-}$ is preferentially extracted over free Sn(II) species even when these are present in much higher concentration.

Rhodium extraction dependence on HCl concentration (0.7M to 8M HCl) in the feed was examined for a 4×10^{-3} M Rh solution having a Sn:Rh molar ratio 12:1. The extraction results are plotted in Figure 4.6. In order to clearly demonstrate the need for a system involving the use of Sn (II), the extraction results for similar rhodium solutions, but containing no tin, are also included in this Figure. For the pure rhodium solutions, the extraction level is low ($D < 1$) throughout the acidity range tested and corresponds approximately to the amount of $RhCl_6^{3-}$ present in solution. For the Rh/Sn solutions, however, very high extraction ($D > 50$) is obtained throughout. The excellent extraction results indicate that for the extraction stage, this system could easily be applied to a wide variety of acid/chloride ion containing feeds.

For practical purposes, since it could happen that solvent extraction would not immediately follow activation, the effect of aging the activated feed on metal extraction was studied and the results are presented in Figure 4.7. In agreement with the results of section 4.2, it was found that quantitative extraction occurred for activated solutions aged at least up to two days, but for solutions aged five days, the extraction level is similar to that of pure Rh-Cl solutions. In terms of extraction, a two-day waiting period between activation and the start of solvent extraction would not be problematic, for the conditions tested here, but in general, the time would depend on the Sn(II) concentration in solution.

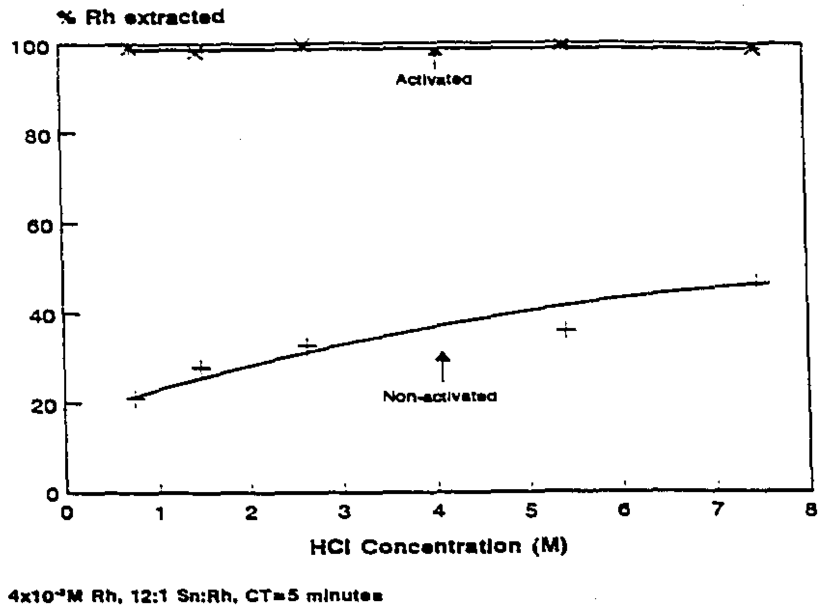


Figure 4.6: Effect of hydrochloric acid concentration on rhodium extraction for both Sn-activated and pure Rh-Cl feed solutions.

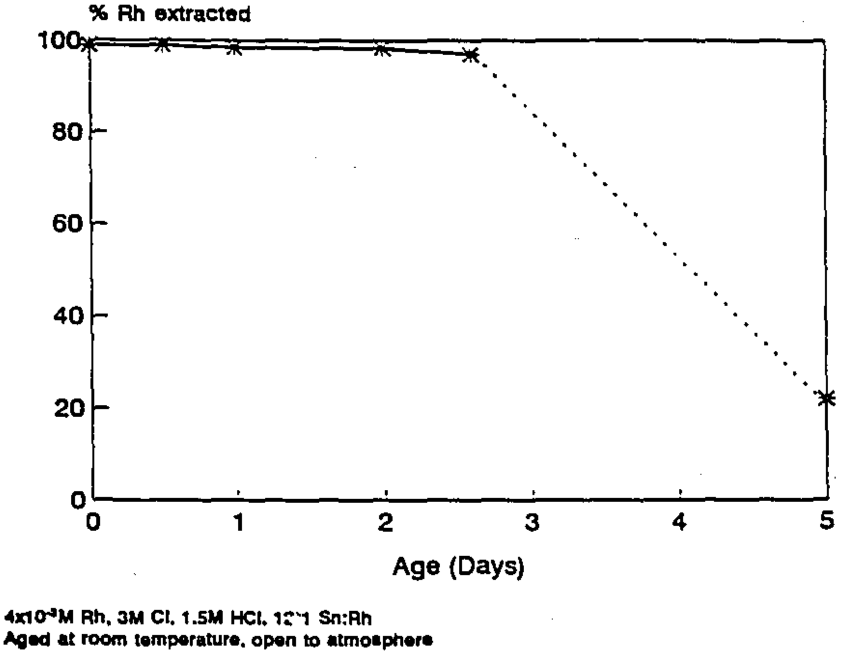


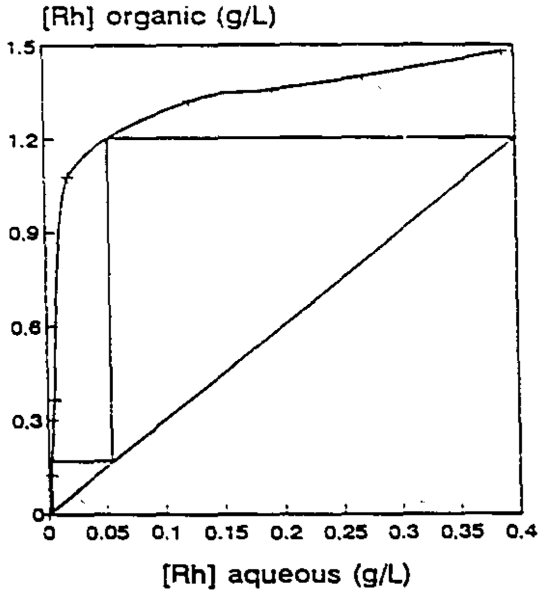
Figure 4.7: Effect of age of activated feed on rhodium extraction.

The extraction isotherm was obtained and a McCabe-Thiele diagram was constructed as shown in Figure 4.8. The extraction isotherm has an extremely sharp rise which represents a very high distribution coefficient and begins to curve off only when nearing fully loaded conditions. Calculations based on mass balance for the fully loaded organic have shown that the Kelex:Sn:Rh molar ratio is 4:5:1. The limiting loading level is in the order of about 1.5×10^{-2}M Rh for a 0.058M Kelex 100 solution (corresponding to 2 vol% [8]). To achieve a higher loading level, it is simply necessary to use a higher concentration of extractant. Figure 4.8 can be used to calculate the number of theoretical counter-current extraction stages required for a given feed at a specified A/O ratio. Assuming that the feed contains 4×10^{-3}M Rh, if an aqueous to organic ratio of three is used, then only two contacts are sufficient to achieve a raffinate containing less than 5 ppm Rh and a loaded organic having 1.2×10^{-2}M Rh.

4.3.2 Extraction Mechanism

Having determined the main extraction characteristics of the system, the extraction mechanism was examined. Kelex 100 can extract via two different mechanisms which are chelate formation, as with Cu(II) or Pd(II) [9,10], or ion-pair formation, as with Pt(IV) [11].

The extraction mechanism of Rh-Sn activated complexes (Sn:Rh > 6) with Kelex 100 has been studied in various ways. First, the ^{119}Sn NMR spectrum of a fully loaded organic phase (loaded with a 12:1 Sn:Rh feed) was obtained and compared to that of the aqueous solution. A magnification of part of the organic spectrum is shown in Figure 4.9. Only one signal was found, a doublet at δ -9.1 ppm (J=620 Hz). Only two of the accompanying satellites can be clearly seen here. This is due to the relatively higher background noise for the organic sample than for the aqueous sample, because of its considerably lower rhodium concentration.



12:1 Sn(II):Rh feed, 1.5M HCl + 0.7M $MgCl_2$
CT = 5 minutes, 0.058M Kelex 100

Figure 4.8: McCabe-Thiele extraction diagram for a 12:1 Sn(II):Rh feed.

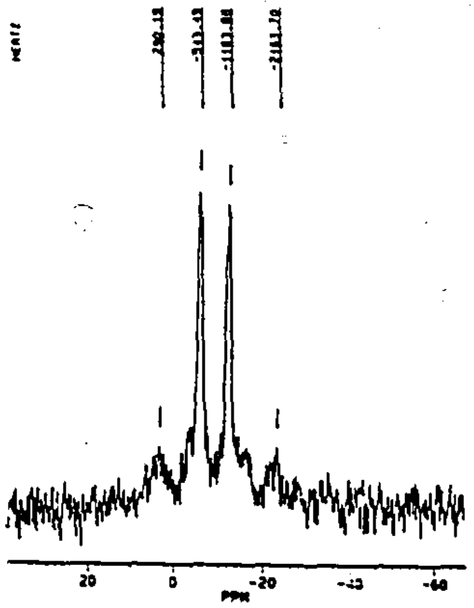


Figure 4.9: ^{119}Sn NMR spectrum of a fully loaded organic solution with 12:1 Sn(II):Rh feed.

It is believed that the signal at δ -9.1 ppm corresponds well to $[Rh^I(SnCl_3)_5]^{4-}$, as in the feed solution. The 13.3 ppm shift in peak position and the 191 Hz change in the coupling constant for the doublet may be due to the significantly different environment of $[Rh^I(SnCl_3)_5]^{4-}$ in the organic phase as opposed to the aqueous phase, rather than to the existence/formation of a different complex. The NMR spectra of Sn(II) complexes are known to be greatly affected not only by the Sn(II) concentration but also by the solvent environment and polarity [12]. The singlet at δ -444 ppm representing free Sn(II) which exists in the aqueous spectrum was not found in the fully loaded organic. This confirms that even under very high loading conditions, $[Rh^I(SnCl_3)_5]^{4-}$ is preferentially extracted over free Sn(II) complexes when the contact time is kept short. In the case of a 12:1 feed, therefore, the Rh-Sn complex, $[Rh^I(SnCl_3)_5]^{4-}$, appears to be extracted via ion-pair formation and exists in the same form in both the aqueous and organic phases. This is in agreement with mass balance which found the fully loaded organic to have a Kelex:Sn:Rh 4:5:1.

During the subsequent stripping tests, it was found that aging, under an open atmosphere, the activated feed for forty-eight hours prior to the start of solvent extraction enhanced the stripping results. Some characterization work, also using ^{119}Sn NMR, of the loaded organics was therefore necessary and the spectrum for an organic fully loaded with a forty-eight hour aged activated feed is shown in Figure 4.10. Contrary to the results of the organic loaded with "fresh" activated solution, which showed only one signal, two signals were obtained here. The strongest was a doublet at -6.7 ppm (J=604 Hz) having four satellites. The location, shape and splitting of this signal indicates that it is still $[Rh(SnCl_3)_5]^{4-}$ and aging does not change the rhodium complex that exists in the organic phase. The other signal was not as prominent and appeared as a singlet at -504.2 ppm. This singlet peak does not appear to be related to free Sn(II), since aqueous solutions of free Sn(II) chlorocomplexes produce signals in the range -370 to -450 ppm, depending on the Sn(II) concentration, and at -402.7 in Sn(II)-loaded organics.

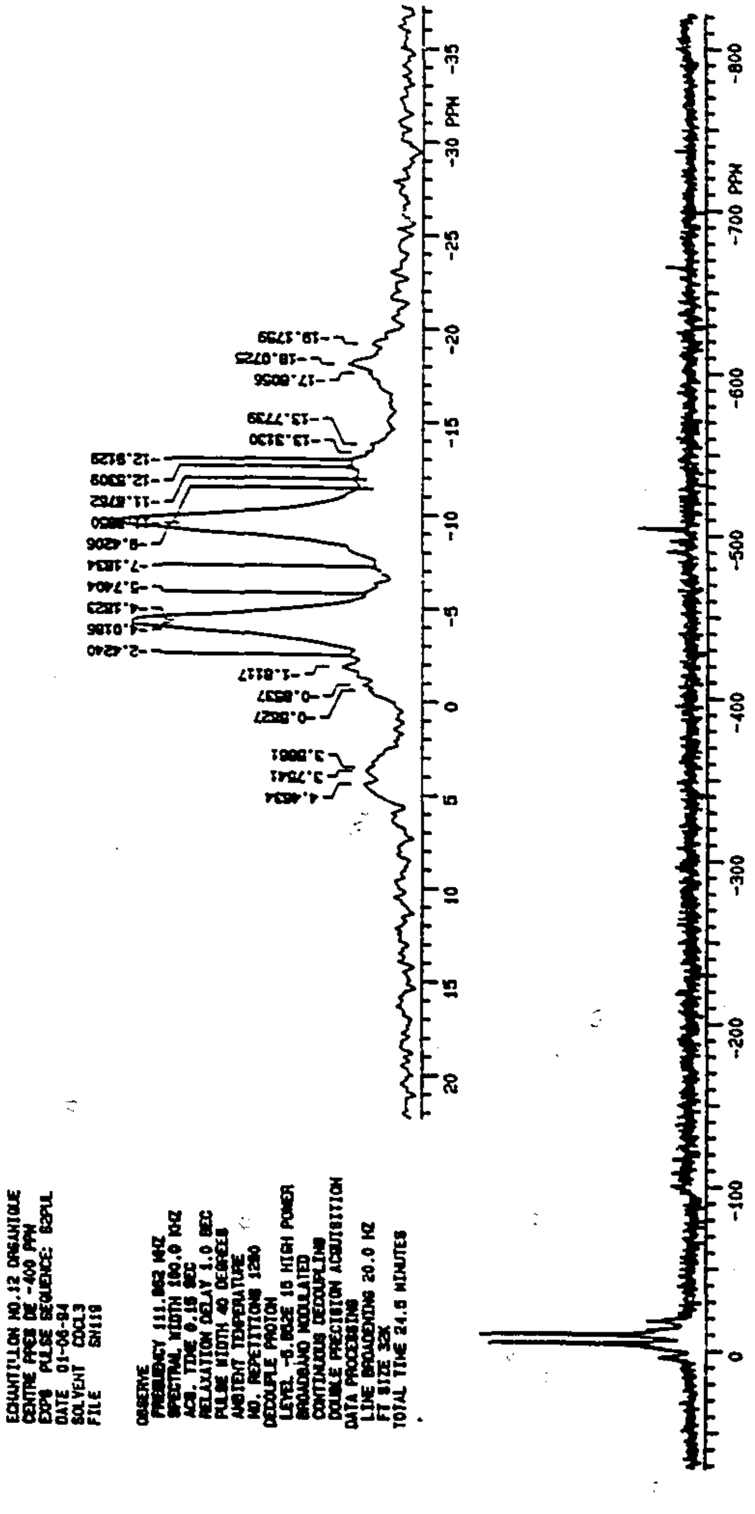


Figure 4.10: ^{119}Sn NMR of a fully loaded organic with 12:1 feed aged fourty-eight hours.

This singlet peak, however, does indicate the presence of another, single tin containing species in the loaded organic. Since it appears only in aged solutions, it may be related to Sn(IV), obtained through the atmospheric oxidation of Sn(II). Some ^{119}Sn NMR studies of Sn(IV) complexes in aqueous solutions place this species near -600 ppm. No reference to organic - Sn(IV) species was found in the literature. It may be that similar to Sn(II), the location of the signal for Sn(IV) is very dependant on concentration and on environment. Sn(IV) has been found, in a previous study [13], to be highly extracted (D > 20) with 7-substituted 8-hydroxyquinolins even under short contact times (three minutes). Chemical analysis of an organic fully loaded with a forty-eight hour aged activated solution showed lower maximum rhodium loading (1.1 g/L) than a fresh solution (1.5 g/L) as well as some co-extracted free tin. The Kelex:Sn:Rh ratio was determined to be 5.4:5.7:1 showing excess tin and Kelex, with the excess ratios equal to two Kelex per tin, corresponding well to ion-pair formation with $SnCl_6^{2-}$.

The ^{119}Sn NMR spectrum of an organic loaded with a forty-eight hour aged feed was also obtained in the non-decoupled mode, to verify for protonation or hydride formation. The spectra of the coupled and non-decoupled mode are virtually identical with both signals appearing at the same ppm, δ-6.7, and without H-splitting. This implies, therefore, that $[Rh(SnCl_3)_5]^{4-}$ is not converted to either a hydride or a protonated complex as has been reported in some other extraction studies [14,15]. It is clear, therefore, that for an aged feed, the extraction still occurs through ion-pair formation of $[Rh(SnCl_3)_5]^{4-}$ but that contrary to a fresh solution, there is some co-extracted free Sn(IV) species even at low contact times.

In addition to ^{119}Sn NMR study, Raman spectroscopy was also used as an analytical tool to verify the extraction mechanism. The Raman spectra of a 12:1 fresh activated feed and of the corresponding fully loaded organic were obtained. In addition, the spectrum of an organic solution previously contacted with 1.5M HCl

+ 0.75M $MgCl_2$ was also obtained. In the range open to the FT-Raman spectrometer used for the activated feed, (> 200 cm^{-1}), only one line was observed at 353 cm^{-1}. Comparison of the Rh-loaded (Figure 4.11b) and acid-loaded (Figure 4.11a) organic phase spectra, showed one extra line at 354 cm^{-1} and another weak one at 164 cm^{-1} for the loaded organic. In addition, none of the other lines changed position or intensity. Once again, it is concluded that the aqueous phase complex, $[Rh(SnCl_3)_5]^{4-}$ is transferred without change through simple ion-pair formation with the protonated organic.

Representing Kelex 100 as HQ, the extraction reactions can therefore be described as:

(i) protonation of extractant:

$$\overline{HQ} + HCl \rightarrow \overline{H_2Q^+Cl^-} \qquad (4.3)$$

(ii) ion-pair extraction of Rh-Sn species:

$$[Rh(SnCl_3)_5]^{4-} + \overline{4H_2Q^+Cl^-} \rightarrow [\overline{Rh(SnCl_3)_5 \cdot (H_2Q)}_4] + 4Cl^- \qquad (4.4)$$

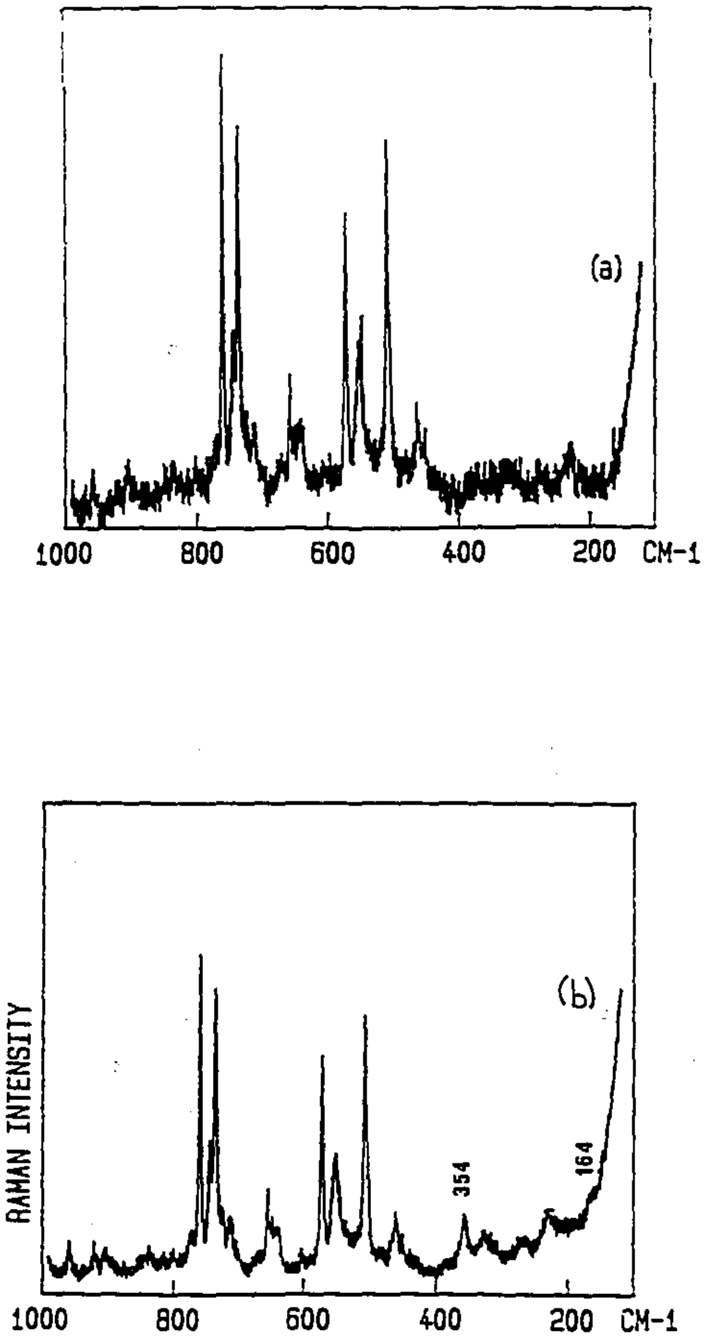


Figure 4.11: Raman spectra of acidic organic solutions; (a) unloaded organic solution; (b) organic solution loaded with 12:1 feed.

4.4 STRIPPING

4.4.1. Identification of an Acceptable Stripping Medium

For most solvent extraction systems, finding a stripping reagent is relatively straightforward. To counteract the extraction reaction, strong acid solutions are used to strip species extracted via chelation, while water, very dilute acids, or basic solutions are used for species extracted via ion-pair formation. For this system, however, although extraction occurs through ion-pair formation, water was found to be an unsuitable stripping reagent. When water and acid solutions of less than 0.3M H^+ were tested as stripping media, a suspended solid was formed in the aqueous phase. This stable mass did not settle even after one week. The precipitate is due to the hydrolysis of Sn(II) which occurs even at relatively high acidity. (K_{sp} of $Sn(OH)_2$ (s) $\approx 5.4 \times 10^{-27}$)[16,17]. Although from these data it appears that hydrolysis should not occur at 0.3M H^+, it is possible that in the organic phase, hydrolysis occurs even more readily. Rhodium and tin analysis of a loaded organic phase, before and after water contact, showed no change in rhodium concentration, meaning that all of the rhodium is maintained in the organic phase, while tin analysis showed that about one third of the tin (1500 ppm) had been released to the aqueous phase. Tin analysis of the clear liquid in the aqueous phase showed only about 500 ppm Sn meaning that much of the tin is present in the precipitate in the aqueous phase. Clearly, solutions of relatively high acidity must be used to avoid solids formation. When solutions of sufficient acidity (0.5M HCl or H_2SO_4) to avoid tin hydrolysis were used, however, no stripping of either rhodium or tin occurred. This is probably because 0.5M H^+ solutions are too acidic to break-up the ion-pair since it has been determined that at this acidity, protonation of the extractant (equation 4.3) already occurs [18,19].

Stripping rhodium from the organic was therefore not as simple as for most systems since an acidic solution is required to avoid tin hydrolysis, while at the same time, an acidic solution cannot break-up the ion-pair to release the rhodium complex.

Stripping coupled with chemical reaction therefore appeared necessary. Remembering also that the primary goal of this project was to develop an industrially attractive system, the stripping media which were screened had to be acceptable from the industry standpoint. A number of reagents were screened and some of the results obtained are shown in Table 4.1. Eventually, it was found that rhodium could be stripped from the loaded organic with a sulfuric acid solution. Unfortunately, stripping is not quantitative in a single contact, and a minimum of three or four consecutive contacts (at A/O=1 and fifteen minute contact time each) are required to achieve high or quantitative stripping. The exact number of stripping contacts required is dependant on the amount of rhodium loaded and can go as high as eight for a fully loaded 0,058M Kelex 100 solution.

Table 4.1: Results of rhodium strip media screening tests

Strip medium	# of contacts	% Rh stripped
0.5M $FeCl_3$ in 1.4M HCl	2	5
0.2M $Fe_2(SO_4)_3$ in 1.4M HCl	2	0
0.4M NH_4Cl in 0.7M HCl	1	0
0.05M EDTA in 0,5M HCl	1	0
1.7M HNO_3	3	20
8M HCl	5	0
1.7M H_2SO_4	5	80
0.5M H_2SO_4 + 3M $(NH_4)_2SO_4$	4	25
1M NaOH	3	20
Cementation with Cu or Zn powder	4 hours, 50°C	0

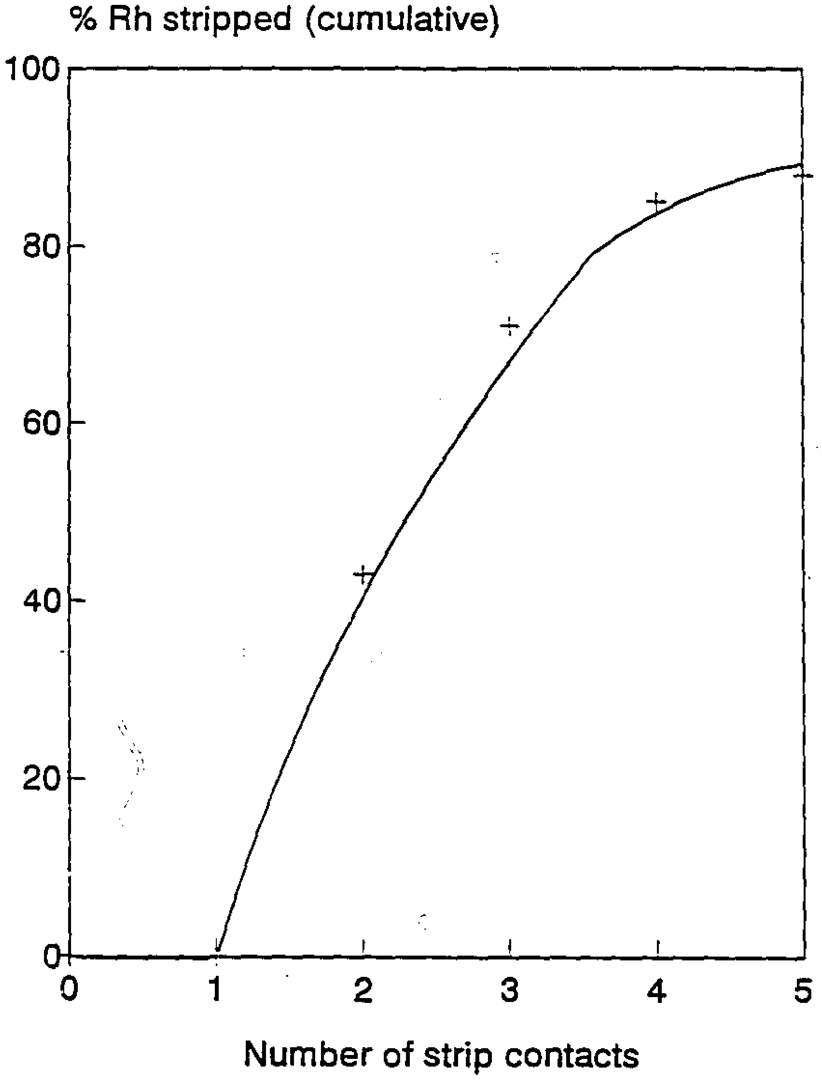
It was expected that the lower the acidity of the strip solution (while still avoiding tin hydrolysis), the better the rhodium stripping. Different acidic sulfate solutions were therefore used on similarly loaded organics and the results are summarized in Table 4.2. Surprisingly, the best results were those obtained with strongly acidic solutions. The 1.7M H_2SO_4 + 1M Na_2SO_4 solution was considered to produce acceptable results and this composition was used for all further stripping tests. Although the stripping kinetics are not shown here, it was clear that stripping increased during the first five minutes of contact time, but that further mixing did not help to achieve higher stripping levels. A contact time of at least five minutes was therefore used for all further stripping contacts. A typical rhodium stripping curve is shown in Figure 4.12. Notice that no rhodium stripping is obtained during the first contact. This peculiar characteristic is explained later. It should also be pointed out here that since sulfuric acid was found to strip rhodium, HCl solutions were also tested as possible strip solutions. No rhodium was stripped with HCl throughout the range tested (0.5 to 8M HCl). Some tin stripping did occur with the 8M HCl solution, but calculations revealed that it is probable that only the free co-extracted tin in the organic was stripped while none of the tin associated with $[Rh(SnCl_3)_5]^{4-}$ was affected.

Table 4.2: Results of rhodium stripping with various sulfate solutions

Strip solution	% Stripped (5 consecutive contacts)
2M $MgSO_4$ in 0.4M H_2SO_4	no stripping
0.8M H_2SO_4 + 1M Na_2SO_4	70
1.7M H_2SO_4	75
1.7 H_2SO_4 + 1M Na_2SO_4	85

4.4.2 Strip Complex Characterization

Only one study was found in the literature referring to the characterization of Rh-Sn complexes in sulfate solutions [20], but this study was for basic solutions where complexes such as $[RhSn_5(SO_4)_7]^-$ and $[RhSn_5(SO_4)_8]^{5-}$ were identified. The complex existing in the strip solution was therefore unknown and it was identified through the combination of a number of techniques.



15:1 Sn(II):Rh in feed, 4x10^{-3M} Rh

Figure 4.12: Stripping of rhodium with 1.7M H_2SO_4 + 1M Na_2SO_4 solution over five consecutive contacts.

Given that $[Rh(SnCl_3)_5]^{4-}$ is the complex which exists in the loaded organic, simple chemical analysis for rhodium, tin and chloride in the strip solution was performed first to determine if the $SnCl_3^-$ ligand follows rhodium in the strip solution. Analysis for rhodium and tin revealed that these elements were always co-stripped at a ratio of 5:1 Sn:Rh (for feeds having Sn:Rh ratios > 6:1). It was also determined that tin still exists as Sn(II) (at least most of it) since it was able to reduce the Rh (I or III) to Rh° upon simple heating of the strip solution to 130°C. If tin had been oxidized to Sn(IV), then the reduction of rhodium would not have been possible as there are no other reductants in the strip solution. Chloride titration, with silver nitrate, of the strip solution was performed and showed a Cl:Sn:Rh of 15:5:1, corresponding to that of the loaded complex, $[Rh(SnCl_3)_5]^{4-}$. However, it was not known definitely at this point whether the $SnCl_3^-$ ligands were still coordinated to rhodium or whether they were replaced by some other ligand such as HSO_4^- and co-stripped independently of rhodium.

Spectrographic characterization of the strip solution was performed with UV spectroscopy and Raman spectroscopy. The UV spectrum of the strip solution is shown in Figure 4.13. The strip solution shows a narrow band at 200 nm and a second band at 300 nm while a 12:1 Sn:Rh feed had bands at 207 and 300 nm (see Figure 4.3f). The similarity would seem to indicate that $SnCl_3^-$ still exists as a ligand, and that the overall strip complex is very close to the complex existing in the activated feed solution, $[Rh(SnCl_3)_5]^{4-}$. The higher magnitude of the band at 207 nm for the activated solution can be easily explained by the presence of excess tin in the activated solution (12:1 Sn:Rh ratio), since pure Sn(II) and Sn(IV) chloride solutions show a single band at 207 nm. A further important observation for the strip solution spectrum is that no band was detected around 250 nm suggesting that no Rh-Cl bonds exist in the strip complex.

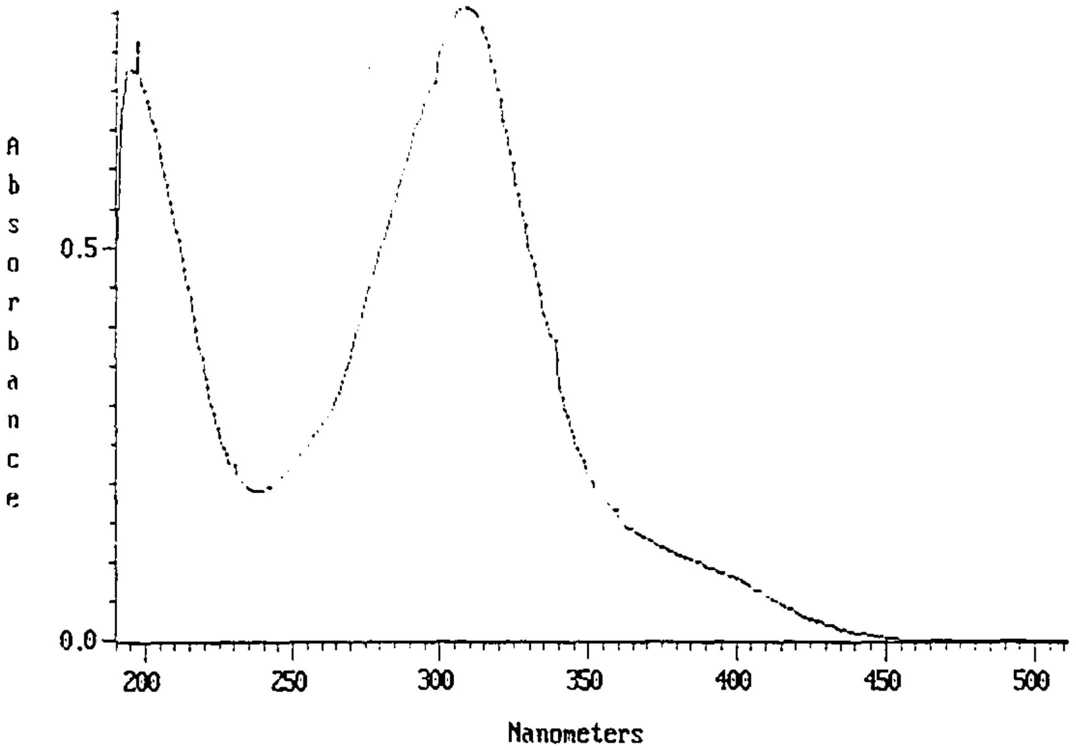


Figure 4.13: UV spectrum of rhodium-containing strip solution.

The Raman spectrum of the strip solution showed two peaks that cannot be attributed to sulfate. One of these is at 334 cm^{-1} and the other is a weaker band at 158 cm^{-1}. Clearly, these are close to those found in the loaded organic, which showed bands at 354 and 164 cm^{-1}. Both signals appear at a lower wavelength and it may indicate that a similar, but not identical, rhodium complex exists.

Since the analysis and spectrographic work was not conclusive, the strip complex was isolated, for further characterization, by the room temperature addition of $(CH_3)_4NCl$ to a strip solution. The addition of this chemical caused the rapid precipitation of the rhodium complex from the strip solution. The precipitate obtained was then filtered and washed . It was redissolved in sulfuric acid and the rhodium, tin and chloride concentrations were once again obtained. The molar ratio 15:5:1 Cl:Sn:Rh was maintained in the precipitate indicating that the five $SnCl_3^-$ ligands are in fact coordinated to rhodium in the strip complex. The precipitate was also redissolved in HCl for sulfate analysis but no trace was detected and therefore, it appears that sulfate is not part of the stripped complex.

Chemical analysis of the CNH content identified three $(CH_3)_4N^+$ groups per rhodium with the likelihood of some waters of hydration. Three $(CH_3)_4N^+$ groups implies that the charge of the complex is 3-. If rhodium had been oxidized to the +III oxidation state, and was therefore octahedrally coordinated, a sixth negatively charged ligand would be required, in addition to the five $SnCl_3^-$ ligands already identified. It is not very likely that this is the case since the sulfuric acid strip solution contains only HSO_4^- and SO_4^{2-} as negatively charged anions and these were not detected in the strip complex. If a hydride were to exist, as reported by some other researchers [6], then a six coordinate complex having 3- charge would be obtained, $[Rh^{(III)}H(SnCl_3)_5]^{3-}$. However, in this situation, it is not likely that a hydride could be formed since the only hydrogen species available in the strip solution are H^+ and these would not naturally be reduced to H^-. If rhodium still exists in the +I oxidation state, then in order to obtain a complex having a negative charge of three, which also contains five $SnCl_3^-$ ligands, a positively charged species is required. If the $[Rh(SnCl_3)_5]^{4-}$ complex were to be protonated, then this would be the case, i.e. $[Hrh(I)(SnCl3)5]^{3-}$. Protonation of $[Rh(SnCl_3)_5]^{4-}$ has been found to occur by one other group of researchers [21] and they have noted that the protonated complex, $[RhH(SnCl_3)_5]^{3-}$ is not dark red but rather yellow. All of the sulfuric acid strip solutions which contained rhodium were indeed yellow and the colour intensity increased with increasing rhodium concentration. When the yellow sulfate strip solutions were diluted with 1M HCl for subsequent atomic absorption analysis, they were found to revert back to reddish tones which could suggest that they were deprotonated in 1M HCl. Hall and Koch [21] were able to detect the presence of the protonated complex in HCl solutions only at concentrations greater than 3M HCl.

To clearly determine the presence of hydrogen in the stripped complex, a ^{119}Sn NMR of the strip solution in the non-decoupled mode was attempted. Since the strip solutions are relatively dilute, however, it proved necessary to concentrate them prior to NMR. This was done by concentration in vacuo at 30°C. It became immediately clear that there is a solubility limit with this complex. All attempts at building the concentration beyond 300 ppm failed. This solubility limit helps to explain why a concentrated strip solution could not ever be obtained and stripping had to be carried out in a number of consecutive contacts, all producing dilute rhodium solutions. The ^{119}Sn NMR of the strip complex could not be obtained as the solutions were too dilute for a signal to appear.

The complex most likely to exist in the strip solution therefore appears to be [Hrh(SnCl3)5]$^{3-}$.

The overall stripping reaction can thus be represented by:

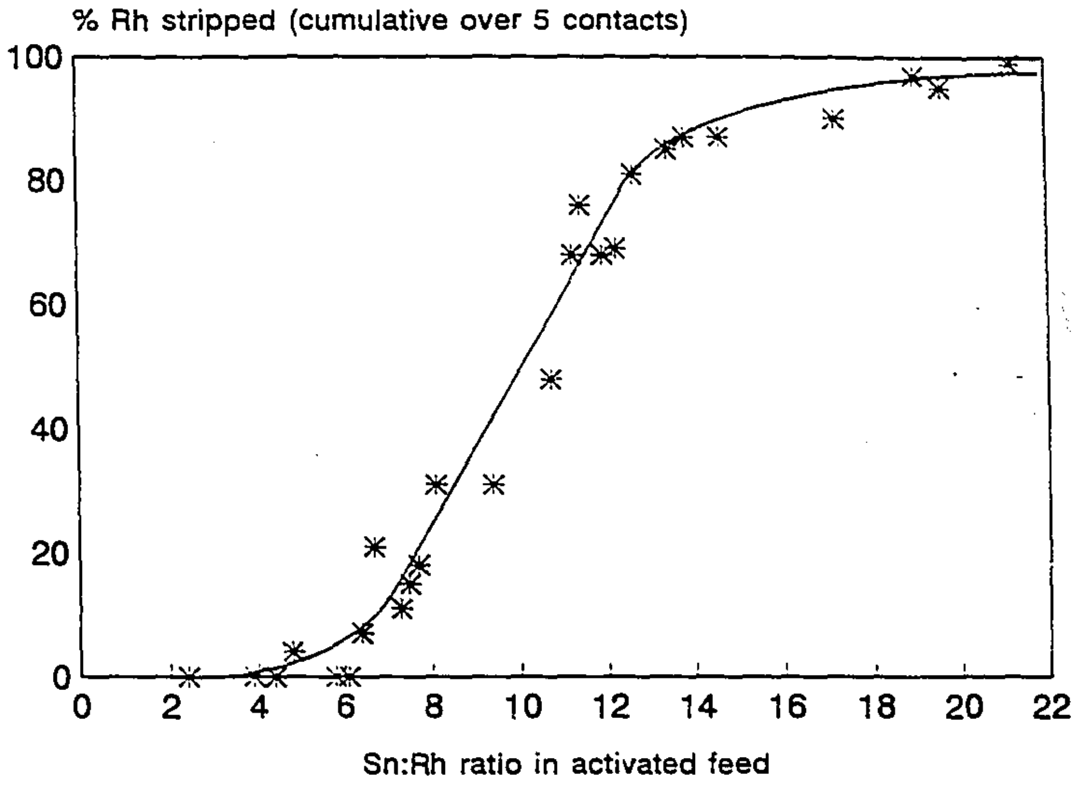
$$Rh(SnCl_3)_5\cdot(H_2Q)_4 + 4HSO_4^- + H^+ \rightarrow RhH(SnCl_3)_5^{3-} + 4H_2Q\cdot HSO_4 \qquad (4.5)$$

4.4.3 Stripping Parameters

While extraction was found to be very efficient throughout a wide range of conditions (acidity, chloride ion concentration, and Sn:Rh ratio), stripping was found to be highly affected by a number of factors. Some of these are directly associated to the conditions of the stripping stage itself, such as the concentration of H_2SO_4, however, the majority are related directly to those which existed in the activated feed or during the extraction stage. The effect of some of the most important parameters and the performance of the system are described below.

The effect of Sn:Rh ratio:

The stripping stage described in this Chapter is effective only for feeds having Sn:Rh ratios $\geq$ 6:1. Figure 4.14 shows the cumulative %Rh stripped (in five consecutive contacts) as a function of the Sn:Rh feed ratio for 4x10^{-3}M Rh solutions. Clearly, under these conditions, stripping is not possible for the complexes of the type $[RhCl_{(6-x)}(SnCl_3)_x]^{3-}$ (where x is less than 6) which exist in solutions having Sn:Rh ratios less than 6:1. Stripping begins in substantial amounts only at ratios higher than 6:1, and therefore, presumably, only for $[Rh(SnCl_3)_5]^{4-}$.



4x10-3M Rh in feeds, 1.5M HCl, 3M Cl
CT=5 minutes, 0.058M Kelex 100

Figure 4.14: Effect of feed Sn(II):Rh ratio on amount of rhodium stripped in five consecutive contacts.

An interesting point in Figure 4.14 is that beyond the 6:1 Sn:Rh ratio, stripping continues to increase. If the same complex exists in both the 6:1 and 20:1 feed solutions, then such different responses to stripping are not expected. The different feeds were therefore studied to ensure that $[Rh(SnCl_3)_5]^{4-}$ is the only dominant complex in all solutions of ≥6:1 Sn:Rh ratios. It was not possible to detect any difference in the complex of 6:1 or 20:1 solutions through any of the techniques used (UV spectroscopy, ^{119}Sn NMR of 12:1 vs 6:1 solutions, and, rhodium, tin and chloride content of the $(CH_3)_4N$ precipitate)[1].

The difference in response to stripping appears to be due to the excess free Sn-Cl complexes present in the higher Sn:Rh solutions. As the Sn:Rh ratio increases, the amount of co-extracted tin also increases and to such a degree that for a 3.5×10^{-3} M rhodium solution, when a 20:1 feed is used, the organic contains virtually no free extractant whereas when a 6:1 solution is used, up to 0.05M of free extractant (90%) exists.

The results of Figure 4.14 were recalculated as stripping degree versus loading level of the extractant and this is shown in Figure 4.15. To calculate the amount of extractant tied up, four Kelex 100 molecules are assumed for every rhodium, $[Rh(SnCl_3)_5 \cdot 4H_2Q]$, and two Kelex 100 molecules are assumed for every tin not associated with the rhodium complex, $[SnCl_4 \cdot 2H_2Q$ or $SnCl_6 \cdot 2H_2Q]$. It is clear from this Figure that the more the organic is loaded, the higher the rhodium that can be recovered during stripping. The presence of free extractant, at the end of the extraction stage, appears to "lock-up" the rhodium.

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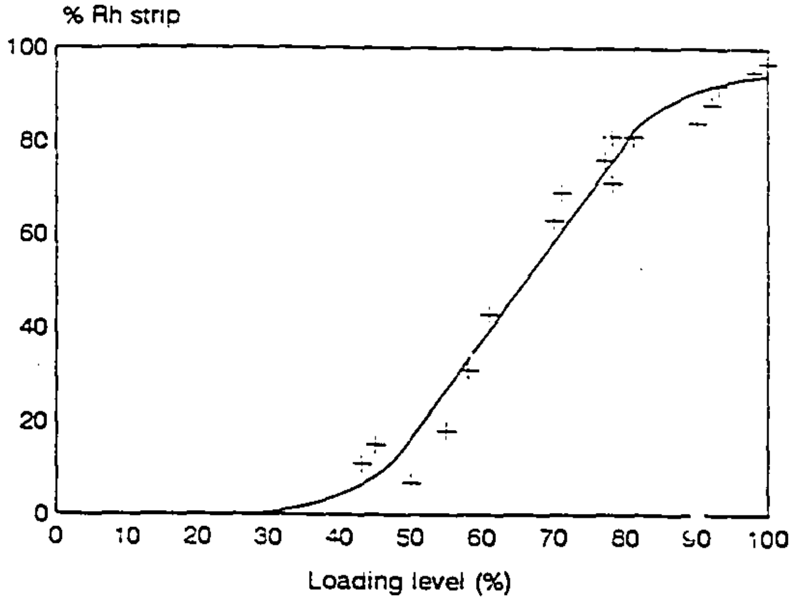
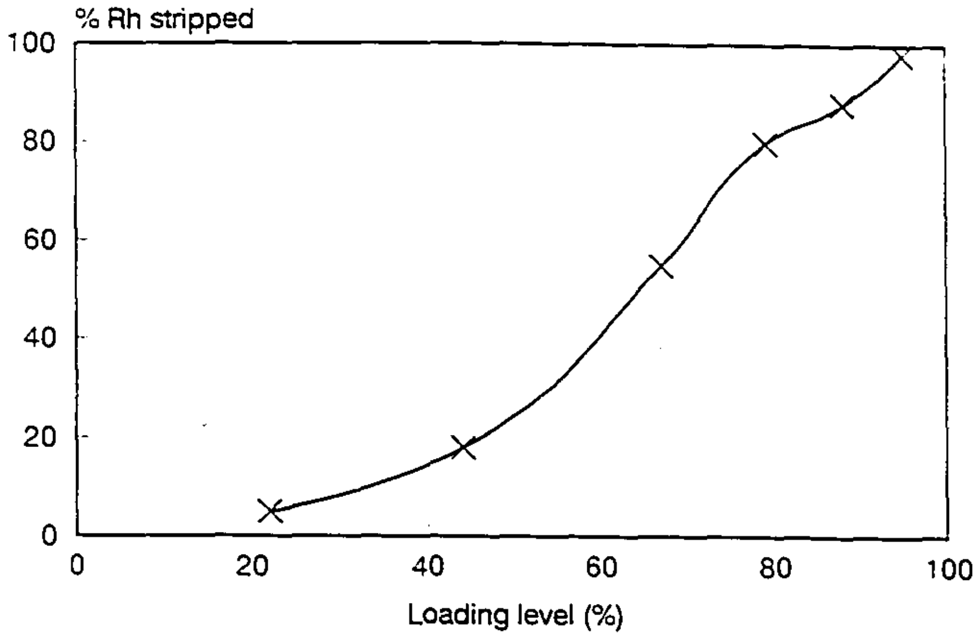
[1] The characterization work is described in section 4.4.2.



4×10^{-3}M Rh, all feeds >6:1 Sn:Rh

Figure 4.15: Effect of organic loading level on amount of rhodium stripped from the organic phase.

Since the rhodium complex appears to be the same in all solutions, whether they be 6:1 or 20:1, and since the degree of stripping appears to be governed by the loading level of the organic, then a 6:1 feed should be strippable if the organic is more fully loaded. Figure 4.16 shows the amount of rhodium stripped as a function of the loading level of the organic for feeds all having between 6:1 to 7:1 Sn:Rh ratio, but having increasing rhodium concentration. A similar curve to that obtained in Figure 4.15 was found, indicating that the loading level is in fact critical and that the rhodium complex is most likely the same in the 20:1 and 6:1 solutions.



4x10-3M Rh feed, all feeds 6-7:1 Sn:Rh

Figure 4.16: Effect of organic loading level on rhodium stripped (all organics loaded with feeds containing about 6-7:1 Sn(II):Rh).

If the loading level is important, then it may be possible that the inability to strip the $[RhCl_{(6-x)}(SnCl_3)_x]^{3-}$ complexes, as shown in Figure 4.14, had more to do with the fact that the organic phase was only about 20% loaded rather than to the complexes themselves. To clarify this point, organics loaded to 55 and 70% with a 2:1 Sn:Rh activated feed were stripped, and 28 and 51% stripping was obtained, respectively, over nine consecutive contacts. It is possible, then, at least in principle, to use this system for all feeds. In the case of solutions having ≤ 6:1 Sn:Rh ratio, it is not experimentally practical to work under fully loaded conditions as this requires very high concentrations of rhodium, as only three Kelex 100 molecules are occupied per rhodium and no excess tin is available to help achieve high loading. It was therefore decided that in order to further evaluate and understand the system from an industrial standpoint, only solutions containing excess tin would be used.

Once again, if the loading level is the feature which governs rhodium stripping, then the same stripping results should be obtained whether the excess extractant, after rhodium extraction, is used to extract excess Sn(II) complexes or any other metal. The effect of co-extracting metals such as Cu(II), Bi(II) and Sn(IV) on rhodium stripping was examined. To calculate the amount of extractant used, four Kelex molecules per rhodium were assumed ($[Rh(SnCl_3)_5 \cdot (H_2Q)_4]$) as well as the appropriate number of Kelex molecules per base element, assuming that they are all extracted via ion-pair formation, with $CuCl_3^-$, $BiCl_6^{3-}$, and $SnCl_6^{2-}$ presumed to be the most dominant complexes in the aqueous solutions [13]. The results are plotted in terms of rhodium stripping as a function of loading level in Figure 4.17. Once more, the same trend is found here, with the highest loading showing the best rhodium stripping.

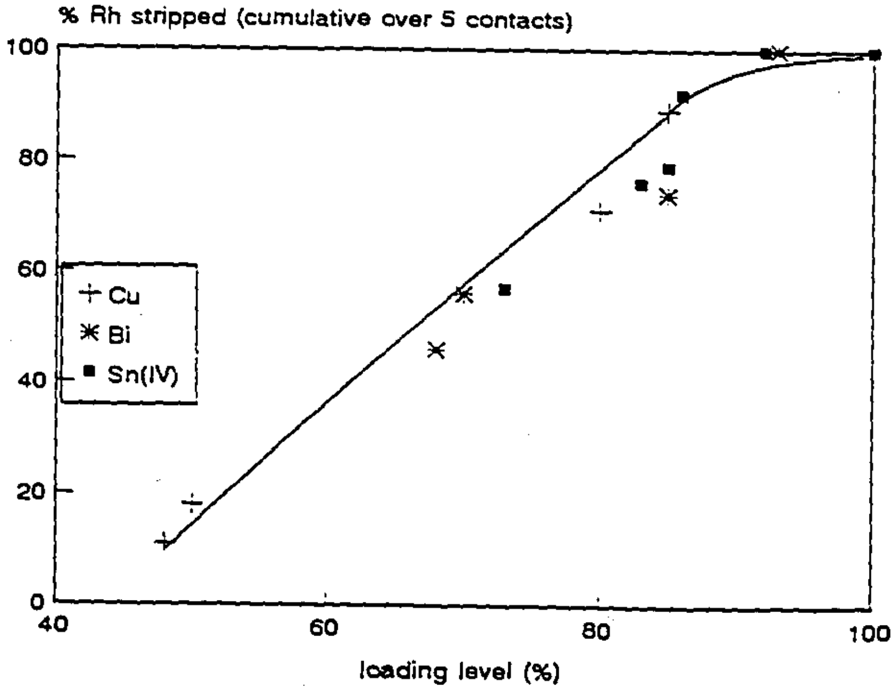


Figure 4.17: Effect of organic loading level on rhodium stripped (organic co-loaded with either Cu, Bi or Sn(IV)).

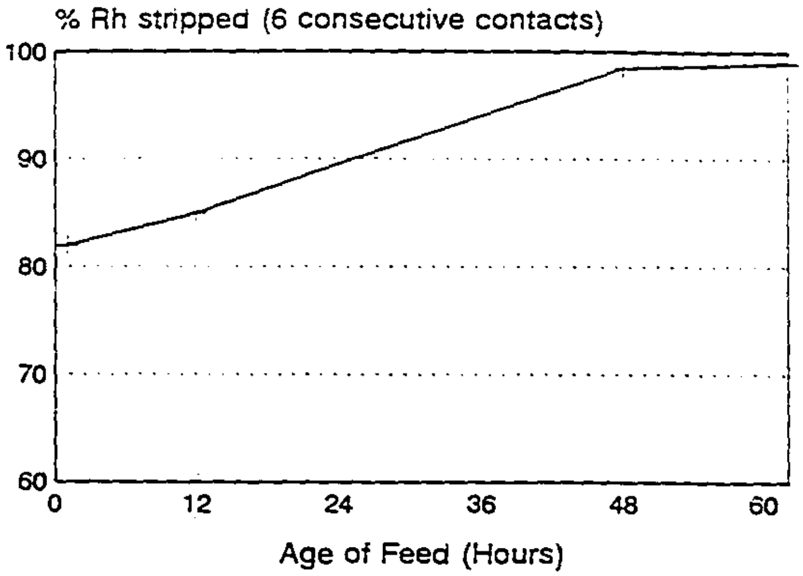
Since, the degree of stripping depends on the loading level, it was of interest therefore, to verify if the amount of rhodium not stripped completely in the case of partially loaded organics was locked-up upon organic recycling. To this end, an organic was used over three consecutive extraction-stripping cycles to determine the potential of rhodium becoming locked in the organic. It was found that for a 4×10^{-3}M Rh solution having a 12:1 Sn:Rh ratio,100 ppm Rh is retained by the organic for each cycle and so if the trend continued, the organic would eventually become saturated with unstrippable rhodium. Similar recycling tests with a 20:1 solution (fully loaded organic) showed no lock-up and 100% stripping was achieved for each of the three cycles.

The effect of activated feed aging:

Similarly as for extraction, the effect of aging the activated feed was tested on rhodium stripping. As reported in sections 4.2 and 4.3.1, the composition and extraction behaviour of the aged solutions does not change, at least up to forty-eight hours. Stripping, however, is affected and Figure 4.18 shows the amount of rhodium stripped as a function of the age of the same activated solution. It was found that aging various activated feeds for about forty-eight hours allowed for quantitative stripping at rhodium concentrations and Sn:Rh ratios where only about 75% stripping could be achieved with a fresh activated feed.

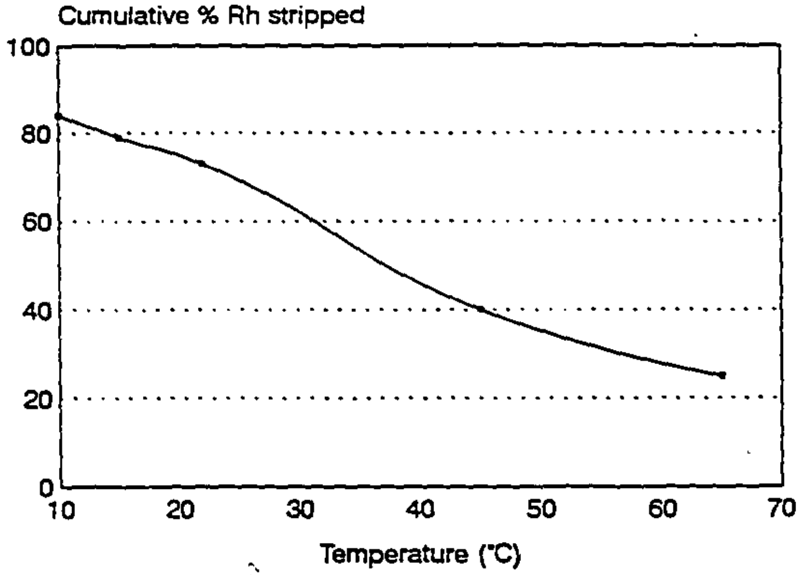
The effect of temperature:

Tests were performed to evaluate the effect of temperature on rhodium stripping. It was hoped that better stripping results would be achieved in fewer contacts by increasing the temperature as high temperature is known to help stripping of other PGM solvent extraction systems [10,11], however disappointing results were obtained. The distribution of rhodium as a function of temperature for five consecutive contacts is displayed in Figure 4.19.



4x10-3M Rh, 3M Cl, 1.5M HCl
Sn:Rh 14:1

Figure 4.18: Effect of age of activated solution on rhodium stripping from loaded organic.



4×10^{-3}M Rh, 3M Cl, 1.5M HCl, 14:1 Sn:Rh,
CT=15 minutes, fresh feed

Figure 4.19: Effect of temperature on rhodium stripping.

From this Figure, it can be seen that stripping decreases with increasing temperature, indicating an exothermic stripping reaction. Nevertheless, even for the low temperatures, it was not possible to concentrate the stripped rhodium in fewer contacts than usual.

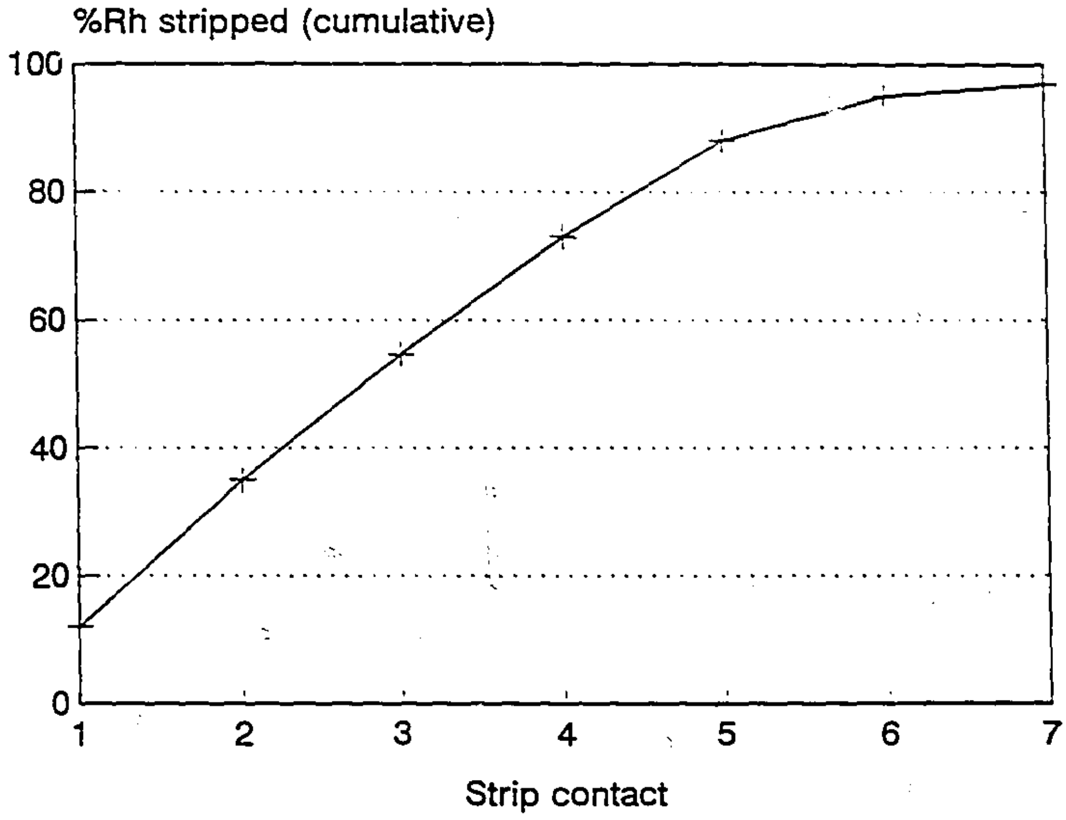
Discussion: The role of chloride ion:

An important point to remember when considering the above stripping results is that they are, generally, for a total of five consecutive contacts. As the rhodium is stripped during each of those contacts, free extractant becomes available and the loading level of the organic is lower. If loading level were the only factor governing stripping, quantitative stripping would never be possible since the last strip contact has much free extractant and very little loaded rhodium. The ability of the free extractant to lock-up the rhodium must therefore have something to do with the way it exists in the organic after the extraction stage and not as it exists after the release of extracted rhodium.

If the extractant does not take part in extraction, then at the end of the extraction stage, it very probably exists in the form of $H_2Q^+Cl^-$. Extractant molecules that had participated in rhodium extraction and have subsequently released rhodium into a sulfate solution, probably exist in the form $H_2Q^+HSO_4^-$. The presence of chloride ion in the organic could then somehow play a role in inhibiting rhodium stripping. In fact, when a strip solution containing about 150 ppm Rh was contacted with fresh extractant, only about 20 ppm were re-extracted. This implies that the stripping reaction is reversible, to some extent, but that the overall distribution favours the aqueous sulfate strip solution (D=0.15). If the organic solution was first contacted with 2M HCl and was therefore in the form of $H_2Q^+Cl^-$, then the rhodium in the strip solution was practically quantitatively re-extracted (D=15). The presence of chloride in the organic somehow inhibits the stripping of rhodium since the presence of $H_2Q^+Cl^-$ causes immediate and complete re-extraction.

A ^{119}Sn NMR spectrum of an organic (loaded with a forty-eight hour aged feed) after the first sulfate strip contact was obtained and examined to further elucidate this feature of the strip reaction. It has been found to be almost identical to that of the loaded organic (shown in Figure 4.10) with the doublet appearing at -7.0 ppm (J=591 Hz), and the singlet at -504.1 ppm. It appears then that the extracted complex does not change after contact with H_2SO_4 and that it is still $[Rh(SnCl_3)_5]^{4-}$. Since the first strip contact does not serve to alter the complex, it must serve another purpose. The first stripping contact seems to serve to condition the organic such that stripping can occur later through the bulk washing out of the co-extracted chloride ions. This phenomenun explains why there is generally no stripping during the first strip contact under non-fully loaded conditions (see Figure 4.17). It is probable, however, that not all of the chloride is removed during the first sulfate strip, otherwise quantitative stripping would always be possible after the first strip contact. When the organic is fully loaded, however, then stripping can start to occur directly in the first strip contact as can be seen in Figure 4.20. This Figure depicts stripping results obtained with a fully loaded organic using a 20:1 Sn:Rh activated feed solution. Figure 4.20 reinforces the assumption that it is the free chloride in the organic that inhibits stripping. It also serves to show that a very large number of contacts are required to achieve full stripping when the concentration of rhodium in the organic is high. In fact, it was never possible to strip more than 250 ppm rhodium in any given single strip. Recycling of a strip solution to build up rhodium concentration also failed to produce concentrated rhodium solutions. This obviously relates to the limited solubility of the back-extracted complex in the sulfate strip solution (see section 4.4.2).

As far as the actual mechanism of the stripping reaction, not much can be said. The proposed stripping reaction (equation 4.5) can only serve to suggest the overall transfer of the Rh-Sn complex from the organic into the strip phase.



loaded organic has 1125 ppm Rh,

Figure 4.20: Rhodium stripping from a fully loaded organic, over seven consecutive contacts, with 1.7M H_2SO_4 + 1M Na_2SO_4.

Despite the evidence gathered with the various characterization techniques used (see section 4.4.2), it is not yet clear how the sulfate medium causes the release of the $Rh(SnCl_3)_5^{4-}$ complex. Is it the protonation of the complex to $RhH(SnCl_3)_5^{3-}$ which somehow occurs in the sulfate medium that causes stripping or simply is it the absence of any free chloride? The latter would seem more plausible. It may be thought that upon the washing out of all free chloride ion with the preceding H_2SO_4 contacts, the $Rh(SnCl_3)_5^{4-}$ complex is at least to a certain degree destabilized due to the dissociation of part of $SnCl_3^-$:

$$SnCl_3^- - SnCl_2^\circ + Cl^- \tag{4.6}$$

This would inevitably cause release of rhodium in the chloride-free sulfate medium and thus stripping could take place. Given that eventually the higher Sn:Rh system had to be abandoned in favour of the low Sn:Rh system (see next Chapter), no further investigations into the stripping reaction were pursued.

Rh recovery from the strip solution:

Recovery of rhodium from the strip solution is simple and can be achieved by heating the strip solution to 130°C. The Sn(II) present in the strip complex reduces rhodium (I and/or III) to Rh° with no co-precipitated tin and a black rhodium powder is obtained. The exact purity of this rhodium metal was not determined. Such powder was obtained from a one litre sample of $1{,}5\times10^{-3}$ M Rh and $8{,}0\times10^{-3}$M Sn(II) sulfuric acid strip solution within five minutes when heated to 130°C.

4.5 SIMPLIFIED SOLVENT EXTRACTION FLOWSHEET

A conceptual flowsheet of the solvent extraction system for rhodium using high ratios of Sn:Rh (>6), Kelex 100 as extractant and H_2SO_4 stripping is presented in Figure 4.21. It is based on the assumption of a 4×10^{-3}M Rh solution and a 0.058M

Kelex 100 organic solution. Activation is carried out first with a Sn(II):Rh ratio of >6:1, preferably about 12:1 . The organic is fully loaded by working with an A/O ratio of three and by performing two consecutive counter-current extractions. The loaded organic then goes to stripping where up to eight consecutive contacts are required. The final concentration of the strip solutions is in the order of 150 to 200 ppm Rh. This strip solutions could then be heated to 130°C and rhodium powder obtained. The organic which has been stripped of rhodium must be scrubbed of tin. This can be achieved with a one hour contact of 1M NaOH [13]. Although it is believed that contacting Kelex 100 with alkaline solutions can cause severe organic degradation, it has recently been shown [22] that when the alkalinity is only 1M NaOH, the degradation is very small. In addition, the contact time in this system is only one hour, for each overall cycle, and the high value of the metal product, rhodium, makes acceptable that some organic degradation would occur. Following tin scrubbing, the organic must be regenerated with a hydrochloric acid solution, and then it is ready to return to the extraction stage.

The flowsheet described above is not industrially attractive. Since a 4×10^{-3}M rhodium solution is used as feed and only a 2×10^{-3}M rhodium solution is produced in the strip solution, the system cannot be described as a process. One of the purposes of solvent extraction is to concentrate a solution in addition to purifying and separating a given element. Work on this system was eventually abandoned as a concentrated strip solution was never achieved. Further work focused on a different stripping method involving low Sn:Rh ratios (about 3:1) and the following Chapter describes this alternative system.

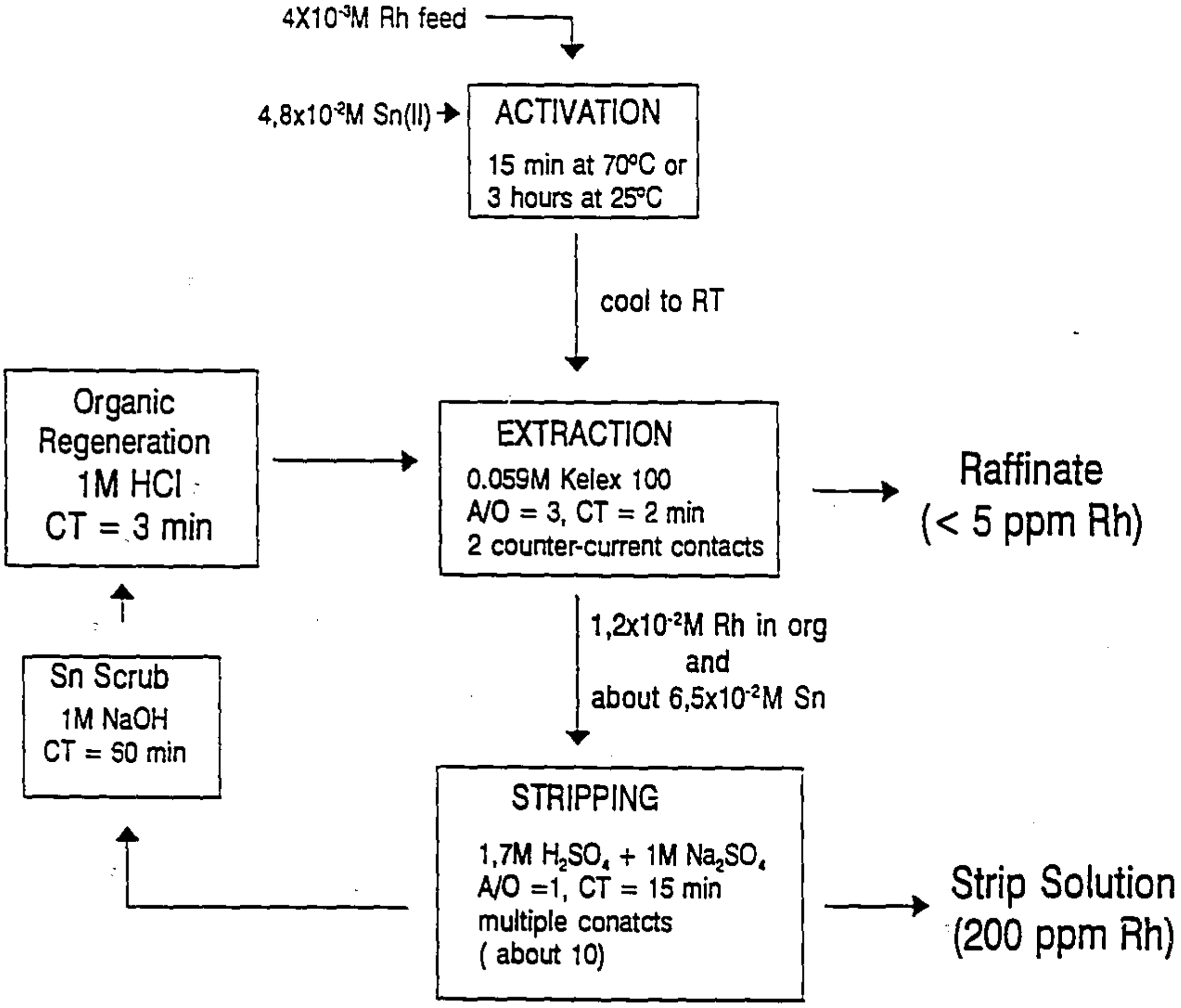


Figure 4.21: Simplified flowsheet of the solvent extraction system based on a 12:1 Sn(II):Rh feed solution, with Kelex 100 as organic extractant and 1.7M H_2SO_4 + 1M Na_2SO_4 as strip solution.

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CHAPTER 5

THE LOW Sn:Rh (<6:1) SYSTEM: EQUILIBRIUM STUDIES

5.1 INTRODUCTION

A solvent extraction system valid for activated solutions having ≥6:1 Sn:Rh molar ratios was described in Chapter 4. That system had its limitations, therefore, work on developing an alternative, better-responding system was initiated. The two main areas in which significant improvements were aimed for included (i) a reduction in the amount of Sn(II) required and (ii) achieving a concentrated strip solution. Work on this system therefore focused exclusively on feeds having a Sn:Rh ratio ≤6:1. Scoping tests on possible stripping media identified sodium sulfite as promising reagent and a thorough study was performed on this system. This study involved both process development type work as well as fundamental work that sought to describe quantitatively the complexes formed, the equilibrium and the kinetics of the system.

To describe this work, a basic overview of the activation stage is given first. The equilibrium extraction results are then presented and the overall extraction reaction and mechanism are identified. Because some of these results are either very similar to or overlap with those of the previous system, these sections are covered in less detail. Next, the stripping stage is discussed through a description of the probable reaction products and of the equilibrium study results. Other important system parameters and flowsheet options which were investigated are also reported. Finally, a general preliminary flowsheet is shown at the end of this

Chapter. The kinetics of the stripping stage of this system are described in Chapter 6.

5.2 ACTIVATION STAGE

As for the previous system, the first stage is activation, which involves the interaction of the rhodium feed solution with stannous chloride. One major improvement aimed for in this system was to diminish the amount of tin required. It had been previously found that quantitative rhodium extraction is possible at a ratio of about 3:1 Sn:Rh (Figure 4.5) and therefore all further work for this system was performed at this ratio. As shown in Figure 2.5, at 3:1 Sn:Rh, the most dominant complex is $[RhCl_3(SnCl_3)_3]^{3-}$ (about 80%) with other minor complexes also co-existing in solution.

The activated feed solutions were briefly characterized to ensure that $[RhCl_3(SnCl_3)_3]^{3-}$ is the main complex that exists in solution. The ^{119}Sn NMR spectrum of a 3:1 Sn:Rh activated solution was obtained and only one signal was found, a doublet at δ -410.2 ppm (J=714 Hz). This corresponds well to the doublet found by Moriyama et al. [1] at δ -411.1 ppm (J=718 Hz), and the complex was confirmed to be $[Rh^{III}Cl_3(SnCl_3)_3]^{3-}$. No other Rh-Sn complexes or free Sn(II) species were detected through ^{119}Sn NMR in the activated feed solution.

For this system, activation was also performed by heating the rhodium chloride feed solution, to which the desired quantity of $SnCl_2$ had been added, at 70°C for fifteen minutes. The activation reaction is extremely rapid. The colour change from pink ($[RhCl_{6-x}(H_2O)_x]^{(3-x)-}$ complexes) to orange ($[RhCl_{6-x}(SnCl_3)_x]^{3-}$ complexes) is complete after as little as five minutes. Because UV spectroscopy cannot differentiate between the different $[RhCl_{6-x}(SnCl_3)_x]^{3-}$ complexes, it could not be used to determine the exact time required for activation at 3:1 Sn:Rh. It is apparent, however, that the reaction could be carried out at room temperature in a reasonably short period of time (probably as little as fifteen minutes). For economic considerations in an industrial setting, room temperature activation should not be overlooked.

For this system, care must be exercised if the activated solution is to be stored because all of the tin exists as $[RhCl_3(SnCl_3)_3]^{3-}$ and atmospheric oxidation of Sn(II) would involve the decomposition of the activated species. It would be preferable, and in some cases necessary, not to store activated solutions for extended periods of time without protection from the atmosphere.

The activation stage, at 3:1 Sn:Rh ratio, can be summarized through the following reaction:

$$RhCl_{6-x}(H_2O)_x^{(3-x)-} + 3SnCl_3^- - [RhCl_3(SnCl_3)_3]^{3-} + (3-x)Cl^- + xH_2O \tag{5.1}$$

$$(\text{where } 0 \leq x \leq 2).$$

The most abundant rhodium and tin complexes in the aqueous solution used here (1.5M HCl + 1.5M $MgCl_2$) are not those written above and equation 5.1 can therefore be rewritten as:

$$RhCl_5(H_2O)^{2-} + 3SnCl_4^{2-} - [RhCl_3(SnCl_3)_3]^{3-} + 5Cl^- + H_2O \tag{5.2}$$

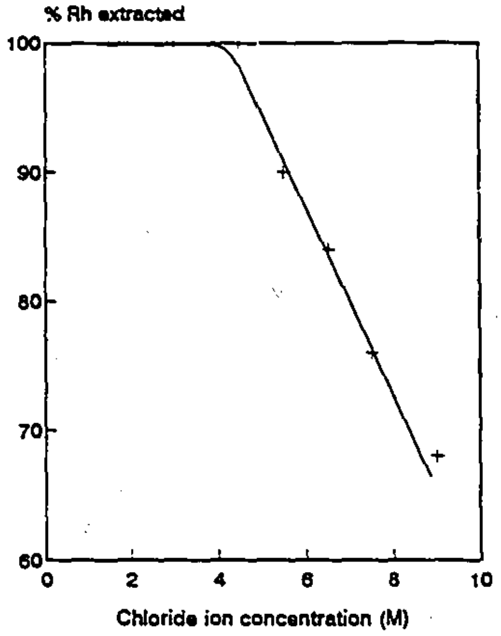
5.3 EXTRACTION STAGE

Once it was established that $[RhCl_3(SnCl_3)_3]^{3-}$ is the rhodium complex in the activated solution, the extraction behaviour of this complex with Kelex 100 was studied through both equilibrium tests and chemical characterization.

5.3.1 Equilibrium Studies

As for the previous system, a contact time of five minutes was also used here, since this was sufficient for quantitative rhodium (and tin) extraction. No excess tin exists, therefore there can be no exchange reaction as there was in the previous system.

The effect, on rhodium extraction, of the feed chloride ion concentration, at a fixed acidity of 1.5M H^+, was studied and the results are shown in Figure 5.1. Although chloride ion does not have a noticeable effect in the lower concentration region (1.5M to 4.5M Cl^-), it does hinder extraction at higher concentrations (4.5 to 9M Cl^-). The decrease in extraction degree can be studied by making use of slope analysis.



Feed: 1.5M HCl + MgCl2, 3.7x10-3M Rh, Sn:Rh=3:1
0.058M Kelex 100, A/O = 1.

Figure 5.1: Effect of chloride ion concentration on rhodium extraction from 1.5M H^+ solutions.

If the extraction reaction is postulated as:

$$[RhCl_3(SnCl_3)_3]^{3-} + \overline{3H_2Q^+Cl^-} \rightleftharpoons \overline{[RhCl_3(SnCl_3)_3\cdot(H_2Q^+)_3]} + 3Cl^- \qquad (5.3)$$

then,

$$K_{ex} = \overline{[RhCl_3(SnCl_3)_3\cdot(H_2Q^+)_3]}[Cl^-]^3 \,/\, [RhCl_3(SnCl_3)_3][\overline{H_2Q^+Cl^-}]^3 \qquad (5.4)$$

so,

$$\log D_{Rh,X} = \log K_{ex} - 3\log[Cl^-] + 3\log[\overline{H_2Q^+Cl^-}] \qquad (5.5)$$

A plot of log $D_{Rh,X}$ versus log [Cl^-] should therefore yield a straight line having a slope of -3. Such a graph is presented in Figure 5.2, where the expected slope was indeed found. In this highly acidic region, all of Kelex 100 is fully protonated [2], i.e. it exists in the form $H_2Q^+Cl^-$ and this explains the good fit of the data. This lends support to reaction 5.3 as written above. The negative effect of chloride ion on the rhodium extraction degree is not noticeable in the lower chloride concentration region because of the large K_{ex} which shifts the equilibrium to the far right.

It was not possible to perform a similar slope analysis study for the effect of Kelex 100 concentration, where a slope of +3 would have been expected. This is because, to perform a slope analysis study, excess extractant would be required to maintain the free Kelex 100 concentration approximately constant, before and after rhodium extraction. In that case, the distribution coefficient would be so high as to render the results much too sensitive for slope analysis. Since there are other simple methods to determine the ratio of extractant molecules per extracted species, reaction 5.3 can be verified through one of these, as shown below.

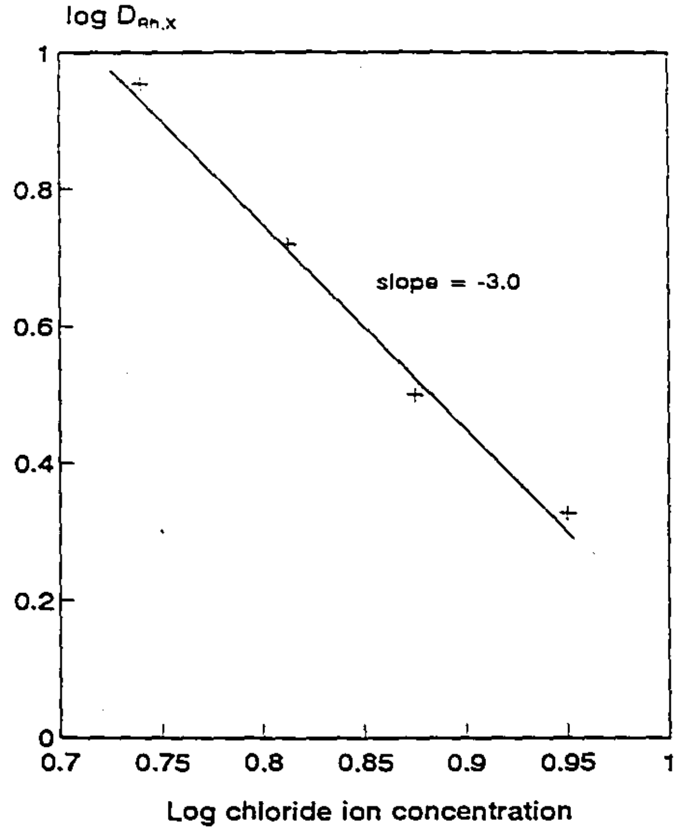
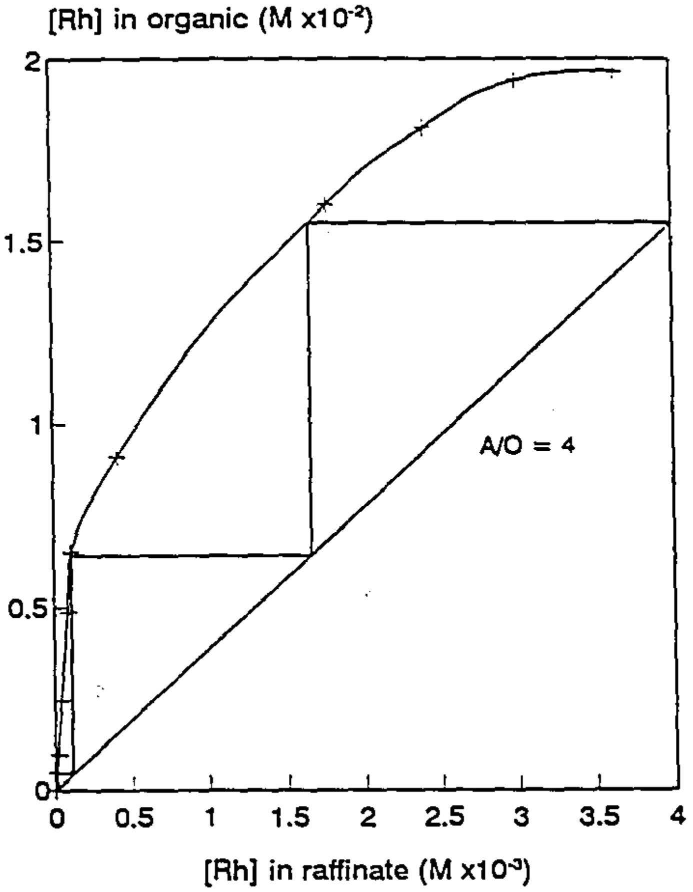


Figure 5.2: Slope analysis for the effect of chloride ion concentration, in the range 4-9M, on rhodium extraction.

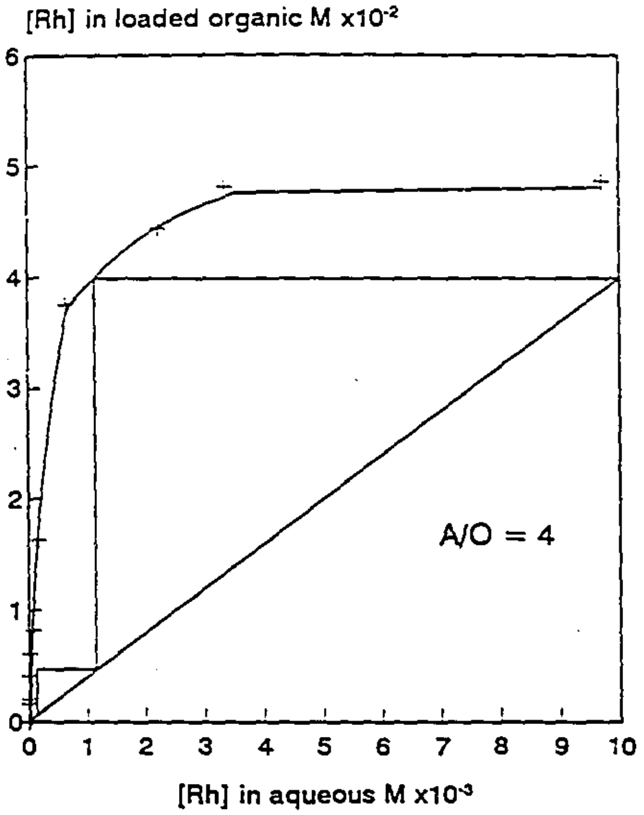
The equilibrium extraction constant was calculated using equation 5.5 and a value of log K_{ex} = 7.06±0.04 was found, signifying very favourable extraction. This, coupled with the fact that extraction is very rapid, makes the extraction stage industrially attractive. The excellent extraction behaviour is also demonstrated in the extraction isotherm below.

Extraction isotherms were obtained and McCabe-Thiele diagrams were constructed, as shown in Figures 5.3 and 5.4, for 0.058M and 0.15M Kelex 100 solutions, respectively. As for the high Sn:Rh system, the extraction isotherms show an extremely sharp rise which represents very high distribution coefficients. The isotherms begin to curve at about 40% loading, but their shape remains very favorable. The maximum rhodium loading level is in the order of about 2.0×10^{-2}M Rh for a 0.058M Kelex 100 solution (corresponding to 2 v% based on total quinoline content [2,3]) and 5.0×10^{-2}M Rh for a 0.17M Kelex 100 solution (5 v%). Calculations based on mass balance for the fully loaded organic have shown that the Kelex 100:Sn:Rh ratio is 3:3:1, for a 3:1 Sn:Rh feed, lending support to reaction 5.3. It should also be pointed out that the Sn:Rh ratio in the loaded organic was always 3:1, whether the organic was 10% or 100% loaded. The extracted complex, therefore, does not change with the degree of loading.



0.058M Kelex 100, 5×10^{-3}M Rh feed, 3.0 Sn:Rh

Figure 5.3: McCabe-Thiele diagram for rhodium extraction with 0.058M Kelex 100.



0.17M Kelex 100, 8.2x10^{-3}M Rh, Sn:Rh=3.50

Figure 5.4: McCabe-Thiele diagram for rhodium extraction with 0.17M Kelex 100.

It can be pointed out that one avantage of this system over the previous one is the increased maximum loading level (2x10^{-2}M as compared to 1.5x10^{-2}M Rh) in the extraction stage. The simple reason is that only three Kelex 100 molecules are required for extraction in this case whereas four were required for the previous system.

Figure 5.3 can be used to calculate the number of theoretical counter-current extraction stages required for a given feed at a specified aqueous to organic (A/O) ratio. Assuming that the feed contains 4x10^{-3}M Rh, if an A/O ratio of four is used, then three counter-current contacts are sufficient to achieve a raffinate containing less than 5 ppm Rh and a loaded organic having 1,6x10^{-2}M Rh. The actual necessity of the third contact is questionable since a slight modification in the shape of the isotherm would show that only two stages are required. An isotherm would have to be performed on a real industrial feed, in any case, to determine the exact requirement and the isotherms shown here serve only as a guide to exhibit the excellent extraction efficiency.

A similar McCabe-Theiele diagram, Figure 5.4, was constructed using 5v% Kelex 100 in which case if an A/O ratio of four is used and a feed concentration of 0.01M Rh is assumed, then a loaded organic containing 0.04M Rh can be achieved in two contacts. These conditions are closer to industrial concentration levels and serve to show that the system functions as well at higher concentrations.

5.3.2 Extraction Mechanism

Having determined the main extraction characteristics of the system, the extraction mechanism was determined. Since $[Rh(SnCl_3)_5]^{4-}$ is extracted via ion-pair formation (Chapter 4), it seemed probable that ion-pair formation would also occur here. The ^{119}Sn NMR spectrum, not shown here, of a fully loaded organic phase (loaded with a 3:1 Sn:Rh feed) was obtained and compared to that of the aqueous solution. Only one signal was found, a doublet at δ -411.6 ppm (J=726 Hz). In the case of a 3:1 Sn:Rh feed, therefore, $[RhCl_3(SnCl_3)_3]^{3-}$ appears to be extracted via ion-pair formation and it appears to exist in the same form in both the aqueous and organic phases. This is in agreement with mass balance which found the fully loaded organic to have a Kelex 100:Sn:Rh molar ratio of 3:3:1.

Raman spectra of a 3:1 activated feed and of the corresponding fully loaded organic also indicate that extraction occurs via ion-pair formation. The Raman spectrum of the feed, shown in Figure 5.5, exhibits three peaks: two major bands at 210 and 362 cm^{-1} and a shoulder at about 170 cm^{-1}. Comparison of the acidic unloaded with the rhodium fully loaded organic spectra (Figure 5.6a and 5.6b, respectively) shows no change in peak position or intensity, except for the appearance of two new bands, at 210 and 362 cm^{-1}, as well as a shoulder at 170 cm^{-1}, in the loaded organic phase spectrum. Even though the peaks have not been assigned, it is concluded that the aqueous phase complex, $[RhCl_3(SnCl_3)_3]^{3-}$ is transferred without change through simple ion-pair formation with the protonated organic.

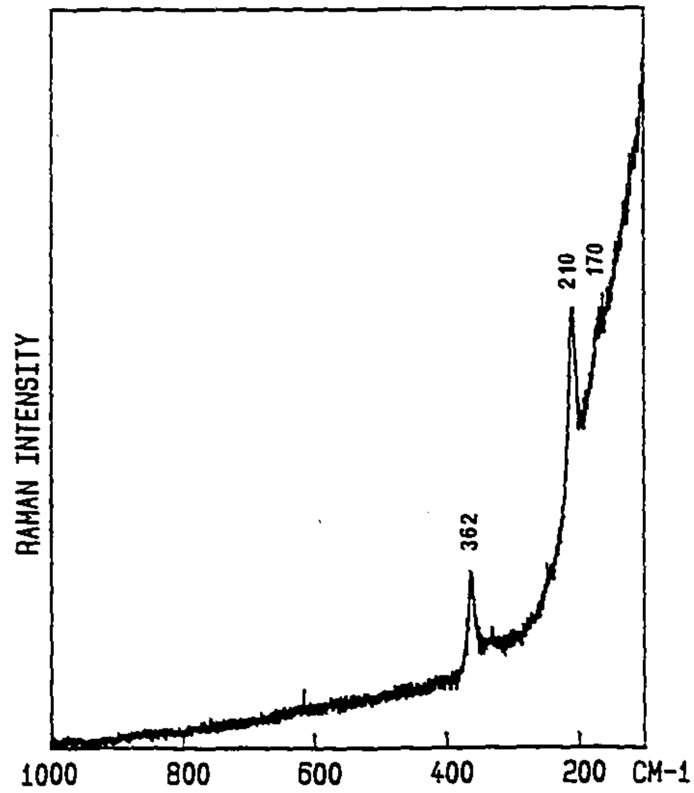


Figure 5.5: Raman spectra of a 3:1 Sn(II):Rh aqueous solution.

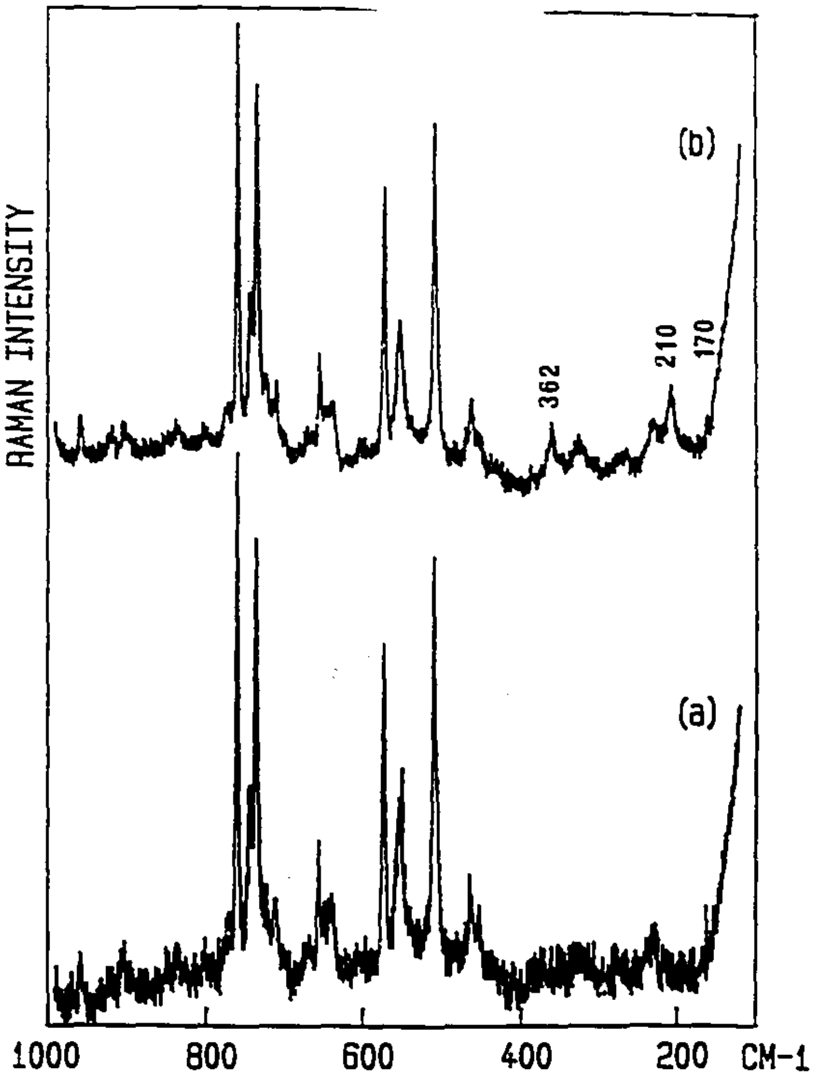


Figure 5.6: Raman spectra of (a) acidic unloaded Kelex 100 solution and (b) Kelex 100 solution fully loaded with 3:1 Sn(II):Rh.

Representing Kelex 100 as HQ, the extraction reactions can therefore be described as:

$$\overline{HQ} + HCl - \overline{H_2Q^+Cl^-} \qquad (5.6)$$

$$[RhCl_3(SnCl_3)_3]^{3-} + \overline{3H_2Q^+Cl^-} - \overline{[RhCl_3(SnCl_3)_3\cdot(H_2Q)_3]} + 3Cl^- \qquad (5.3)$$

5.4 STRIPPING STAGE

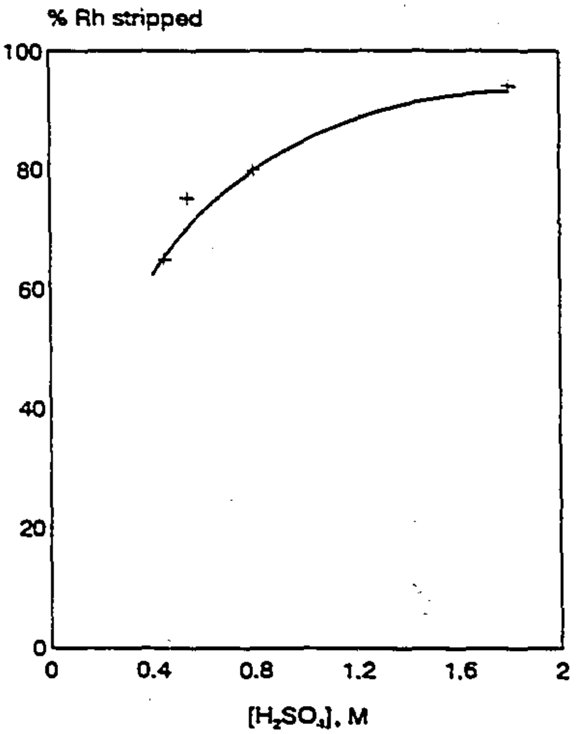
5.4.1. Identification of an Acceptable Stripping Medium

Similarly to the case of the previous system, water could not be used as stripping reagent since tin is co-extracted along with rhodium and could be prone to hydrolysis. In fact, when stripping with water was attempted, a colloidal suspension in the aqueous phase and at the aqueous/organic interface was obtained. Also, given the high stability of the extracted complex (high K_{ex}), it is understandable that simple pH adjustement is not sufficient to provoke the release of the rhodium complex from the organic phase, but that stripping coupled with chemical reaction appears necessary. Because rhodium and tin can both exist in two different oxidation states, it was decided to investigate either reducing or oxidizing agents to destabilize the extracted complex, $[RhCl_3(SnCl_3)_3]^{3-}$, and favour stripping of rhodium from the organic. Some of the results of the scoping work are summarized in Table 5.1.

Table 5.1: Stripping results for scoping tests on the identification of a stripping medium. All loaded organics contain about 4×10^{-3}M Rh and a 3:1 Sn(II):Rh ratio.

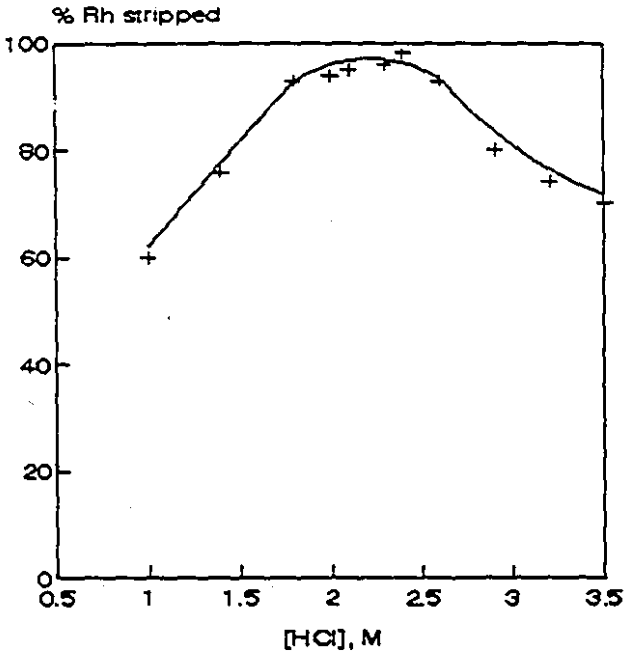
Strip medium	# of contacts (time)	% Rh stripped
1M $FeCl_3$ in 1.5M HCl followed by two 0.5M HCl contacts	1 (two hour) and 2 (fifteen minutes)	0
1M $FeCl_3$ in 1.5M HCl at 60°C	1 (one hour)	0
0.5M $Fe_2(SO_4)_3$ in 1.5M HCl followed by two 0.5M HCl contacts	1 (two hour) and 2 (fifteen minutes)	0
0.05M $K_2Cr_2O_7$ in 3M HCl	5 (twenty minutes)	43 (plateau)
0.25M $K_2Cr_2O_7$ in 3M HCl	1 (twenty minutes)	org. decomposition
0.5M Na_2SO_3 in 1.8M H_2SO_4	3 (twenty minutes)	94
0.5M Na_2SO_3 in 2.4M HCl	2 (twenty minutes)	100

Clearly, sodium sulfite in acidic solutions produced the most promising results. Both sulfuric and hydrochloric acid solutions were initially investigated. The effect of the concentration of both sulfuric and hydrochloric acid on rhodium stripping with 0.5M Na_2SO_3 is reported in Figures 5.7 and 5.8, respectively. Sulfuric acid shows good stripping, but quantitative stripping in a single contact is not possible. In addition, phase separation was problematic in some cases when using sulfuric acid, but not when using hydrochloric acid. It was quickly determined that hydrochloric acid solutions of sodium sulfite gave the best overall results. With hydrochloric acid, a peak can be observed at about 2 to 2.5M HCl where high ($D_{Rh,S}$>10) rhodium stripping is possible. Combinations of HCl with chloride salts were also initially investigated, but for simplicity, it was preferred to retain the as efficient strip medium of 2.4M HCl. The strip solution which was used for all further tests was 0.5M Na_2SO_3 in 2.4M HCl.



3.2:1 Sn:Rh, 4.3x10^{-3}M Rh in organic, CT=20 min

Figure 5.7: Effect of sulfuric acid concentration on rhodium stripping with 0.5M Na_2SO_3.



3.4:1 Sn:Rh, 3.5x10^{-3}M Rh in organic

Figure 5.8: Effect of hydrochloric acid concentration on rhodium stripping with 0.5M Na_2SO_3.

Rhodium stripping was found to increase with increasing sodium sulfite concentration, as shown later in section 5.4.3, however, the reason for which a 0.5M solution is used rather than a more concentrated one is simply because this is the maximum level which can be dissolved without significant formation and loss of SO_2(g).

5.4.2. Characterization of the Stripped Complex

Before the stripping stage is described in further detail, it is important to identify the stripping reaction and the products formed. The rhodium complex was identified through a number of techniques.

Direct chemical analysis for rhodium and tin in the strip solution showed that, contrary to the high Sn:Rh system, tin does not follow rhodium to any significant degree. Chloride determination could not be performed because of the high background level of chloride ion from the 2.4M hydrochloric acid. It is clear, nevertheless, that a rhodium complex different from that in the loaded organic exists in the strip, since it contains very little tin. To identify the new species, the complex was isolated through the addition of ethanol directly into the strip solution. This reduced the solubility of the rhodium complex and a precipitate was collected, filtered and washed (with ethanol).

The infrared spectrum of the precipitate, shown in Figure 5.9, was obtained to detect and identify an SO_x group in the complex. SO_x functional groups respond well to infrared spectroscopy and much information can be obtained from spectra of such complexes by observing the region 500 to 1300 cm^{-1}. The spectrum obtained for the precipitate is shown in Figure 5.9. Clearly, due to the large number of bands between 500 and 1200 cm^{-1}, an SO_x group does appear to form part of the compound. By comparison with known characteristics, it was determined that the functional group could not be either SO_4^{2-} [4] or SO_2 [5] but that the peaks did correspond well to SO_3^{2-} [6] containing compounds. For example, $K_4[IrCl_3(SO_3)_2]$ was found to exhibit four groups of bands at (i) 506, (ii) 612 and 652, (iii) 927, and (iv) 1054, 1078 and 1164 cm^{-1} [6]. The location of the bands in the iridium complex correspond quite well to the bands found for the strip complex at (i) 518, (ii) 658 and 692, (iii) 962, and (iv) 1089, 1113 and 1195 cm^{-1}. Although there are only a limited number of rhodium sulfite complexes reported in the literature, the existence and characterization of $K_3[Rh(SO_3)_3]\cdot 2H_2O$ [7] does confirm that such complexes are possible.

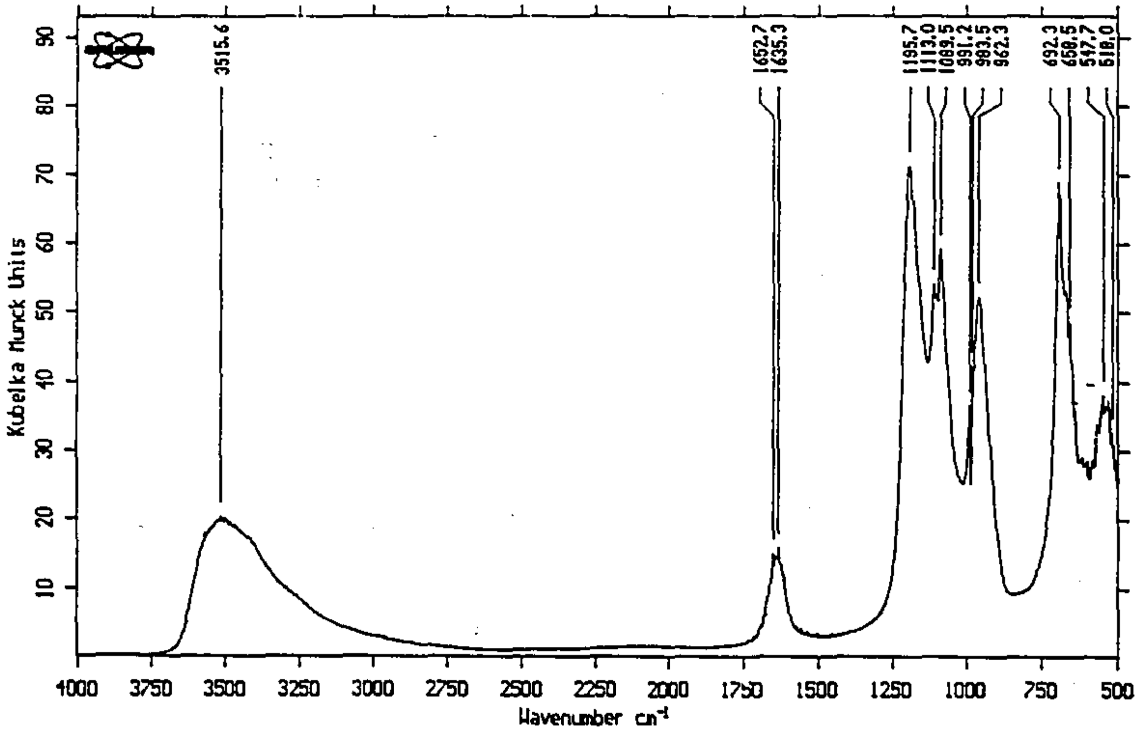


Figure 5.9: Infrared spectrum of the strip solution complex.

The iridium complex mentioned above was described as having the sulfite group as bidentate coordinated [6]. Although infrared was previously believed to be able to identify how a sulfite group is bound, bidentate or chelating and through sulfur or oxygen, there is now some uncertainty about the validity of such determinations [8]. A bidentate complex is also assumed here, but this structure is based on the combination of a number of factors, described below, and not solely on the infrared spectrum.

The chemical content of rhodium, chloride, tin and sodium in this precipitate was determined by redissolving it in aqueous media such as dilute H_2SO_4 or HCl. The sulfur content of the solid was also determined. Through these results, a possible rhodium complex was identified and it is shown in Figure 5.10. Table 5.2 lists the experimental chemical content analysis results and compares them to the theoretical content of the structure proposed in Figure 5.10.

Table 5.2: Elemental analysis results for the strip rhodium precipitate.

Element	Theoretical content	Experimental content
Rh	21.7 (wt %)	20.5 (wt %)
S	13.5 (wt %)	13.8 (wt %)
Cl	2:1 Cl:Rh	2:1, 2:1, 2:1, 2:1, 3:1
Na	3:1 Na:Rh	2:1, 3:1, 3:1, 4:1
Sn	0	0
H_2O	4:1 H_2O:Rh	3.7

The results of Table 5.2 show good agreement between the theoretical and the experimental contents, lending support to the structure shown in Figure 5.10. Although sulfite solutions are generally considered to be reducing, rhodium is still believed to be in the III oxidation state, since it is stable as Rh(I) only in the presence of π-donor ligands [9].

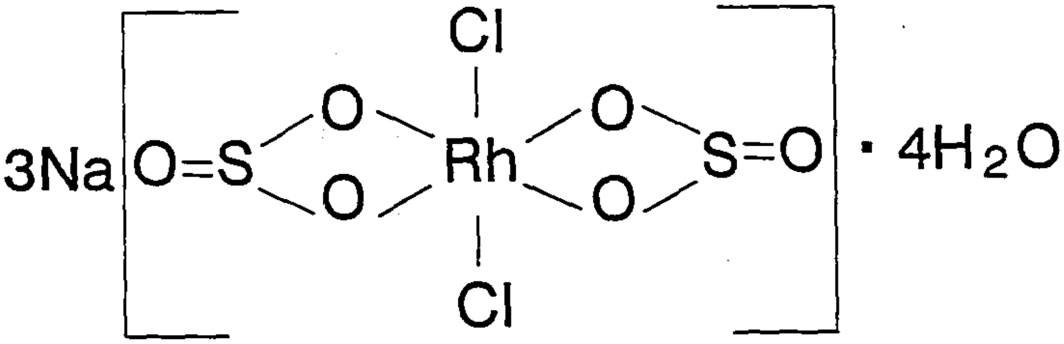


Figure 5.10: Proposed rhodium complex precipitated from the sulfite strip solution.

The water content of the precipitate was only obtained approximately, by heating a solid sample at 110°C over two hours and weighing to measure the weight loss. It was assumed that the only volatile species would be the water, and not any of the SO_3 groups. In order to verify this assumption, an infrared spectrum of the heated precipitate was obtained and still showed the presence of the sulfite group.

During sample preparation for infrared spectroscopy (grinding of the sample) it was found that the solid is quite hygroscopic. Water bands were indeed visible in the infrared spectrum at 3516 and 1635 cm^{-1}, confirming that waters of hydration are present in the solid compound [10]. The exact number of waters of hydration might increase with time if a precipitate were left to stand under atmospheric conditions, but in this study, after filtration and washing, the solid samples were left to dry in the filter paper and were then transferred and stored in a dessicator. To further support the complex of Figure 5.10 as existing in the strip solution, some of the results obtained from the equilibrium study of the stripping stage are described below.

5.4.3. Equilibrium Stripping Stage Studies

Before the equilibrium results are presented, it is worth mentioning that the effect of contact time on rhodium stripping was studied and a contact time of twenty minutes was found to be sufficient to achieve equilibrium levels, and under optimum conditions, quantitative rhodium stripping. A study of the kinetics of the stripping stage was performed and is described separately in Chapter 6.

Because the strip solution contains dissolved sulfite, it also contains some amount of dissolved $SO_2(g)$. A titration was performed to verify that the total sulfite content would not decrease with time, through the atmospheric loss of SO_2 (g) or through the oxidation of SO_3^{2-} to SO_4^{2-}. The sulfite concentration for a strip solution contacted over three cycles, for thirty minutes each time, was found to still be 0.5±0.02M.

Having postulated the main stripping reaction product, $[RhCl_2(SO_3)_2]^{3-}$, and having determined that tin does not follow rhodium into the strip solution to any significant degree, the stripping reaction can be written as follows, for solutions having an acidity of about 2.4M HCl:

$$\overline{[RhCl_3(SnCl_3)_3\cdot(H_2Q)_3]} + 2HSO_3^- - [RhCl_2(SO_3)_2]^{3-} + 2H^+ + Cl^- + 3\overline{[SnCl_3\cdot H_2Q]} \qquad (5.7)$$

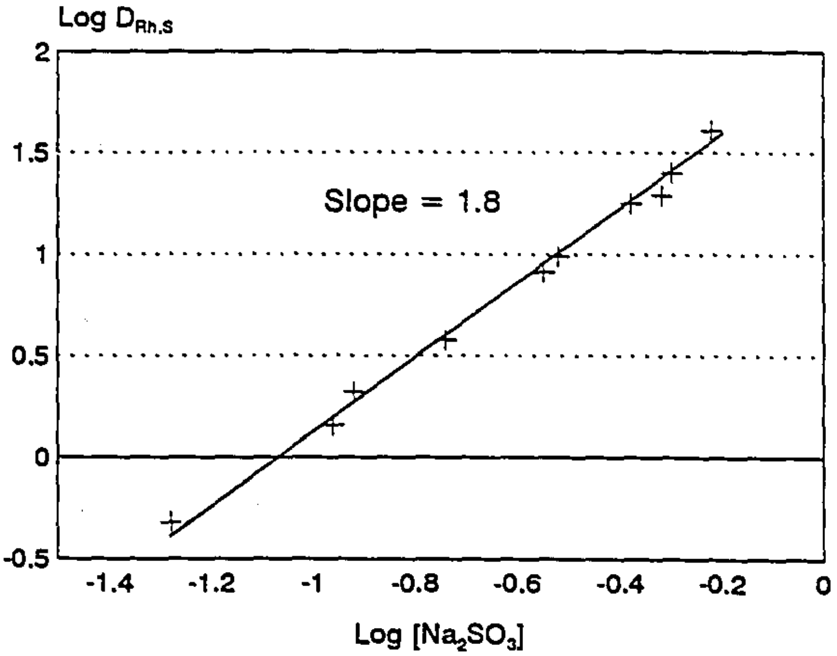
It was not determined, during the course of this work, whether the tin remains extracted as an ion pair of $SnCl_3^-$, or whether it reequilibrates in the 2.4M HCl strip solution to transform to an ion-pair involving $SnCl_4^{2-}$.

From reaction 5.7, the following mathematical expression can be written:

$$\log D_{Rh,S} = \log K_{Rh,S} + 2\log[HSO_3^-] - 2\log[H^+] - \log[Cl^-] - 3\log[SnCl_3\cdot H_2Q] \qquad (5.8)$$

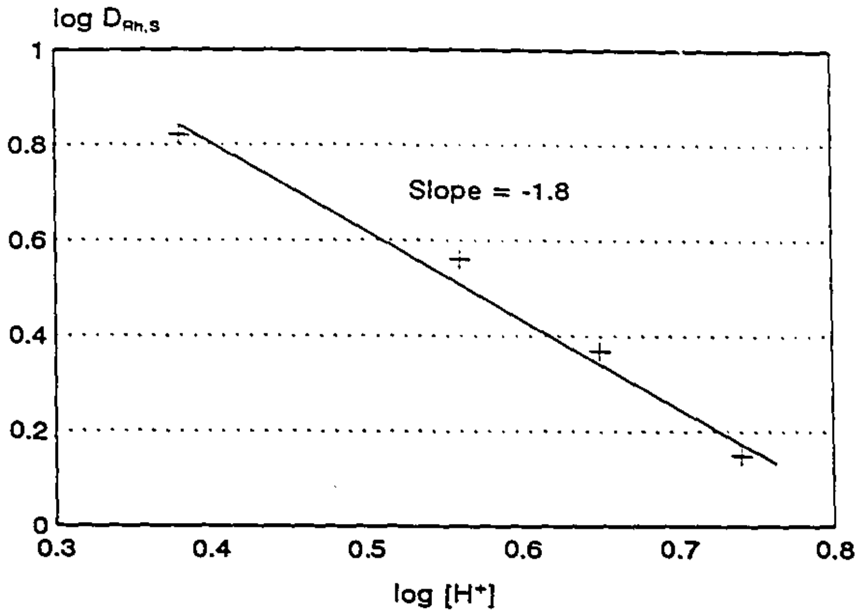
Equation 5.8 can be used to interpret experimental data, similarly as was done for the extraction reaction.

To verify reaction 5.7 and equation 5.8, the stripping distribution coefficient for rhodium, $D_{Rh,S}$, was studied over the following range of conditions: [Na_2SO_3] from 0.05 to 0.65M, [H^+] from 2.4 to 5.5M, and [Cl^-] from 2.4 to 6.6M. Figures 5.11 to 5.13 show the log $D_{Rh,S}$ - log concentration plots for the effects of [Na_2SO_3], [H^+] and [Cl^-], respectively. Straight lines of slopes 1.8, -1.8 and -1.1 were obtained, supporting the stripping reaction as written in equation 5.7.



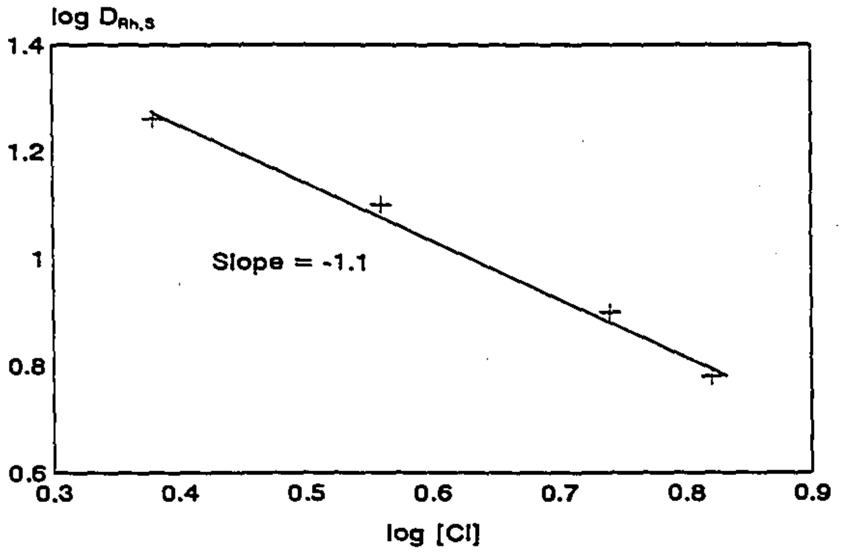
2.4M HCl, 3:1 Sn:Rh, 4.4x10^{-3}M Rh in org, 0.058M Kelex 100

Figure 5.11: Slope analysis plot for the effect of sulfite concentration on rhodium stripping.



in 0.5M Na_2SO_3 and 6.6M Cl^-, 3:1 Sn:Rh, $7.5x10^{-3}$ ppm Rh in org

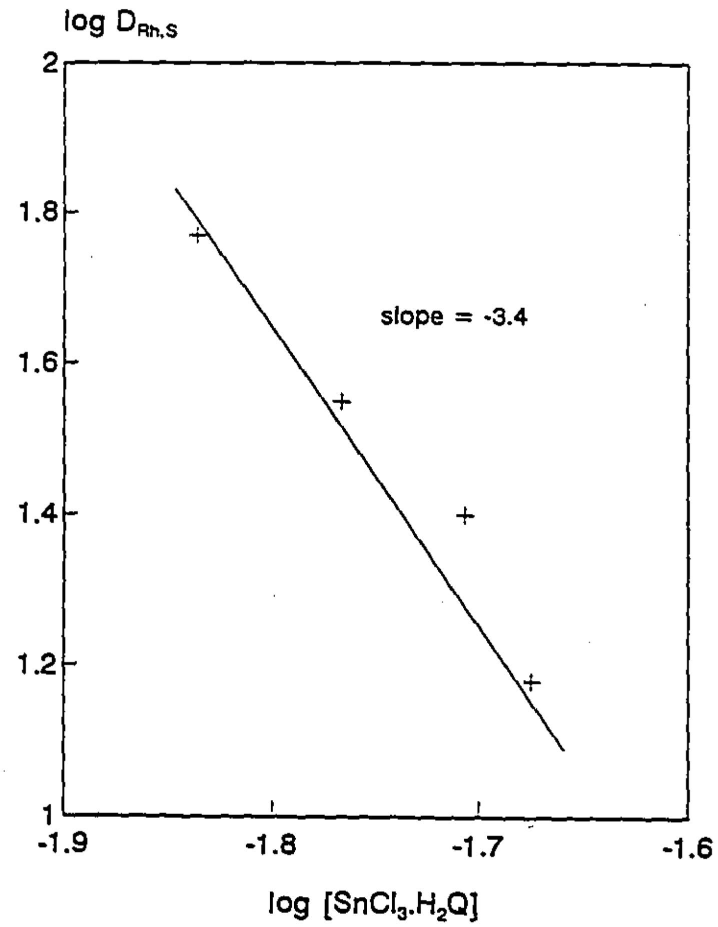
Figure 5.12: Slope analysis plot for the effect of acidity on rhodium stripping.



in 0.5M Na_2SO_3 and 2.4M H^+, 3:1 Sn:Rh, 7.5 $x10^{-3}$M Rh in org

Figure 5.13: Slope analysis plot for the effect of chloride ion concentration on rhodium stripping.

The effect of the equilibrium concentration of $SnCl_3 \cdot H_2Q$ was also investigated. In this case, an organic was first contacted with a solution of $SnCl_2$ and the Sn-loaded organic was then used for the normal extraction and stripping stages. This ensured that some background level of $SnCl_3.H_2Q$, over and above that obtained through stripping alone, would be achieved. The results obtained are shown in Figure 5.14. A slope of -3.4 was obtained, also in agreement with equation 5.7.



stripped with 0.5M Na_2SO_3 in 2.4M HCl, 3:1 Sn:Rh, $8{,}0 \times 10^{-3}$M Rh in org

Figure 5.14: Slope analysis plot for the effect of the concentration of Sn-loaded Kelex 100 on rhodium stripping.

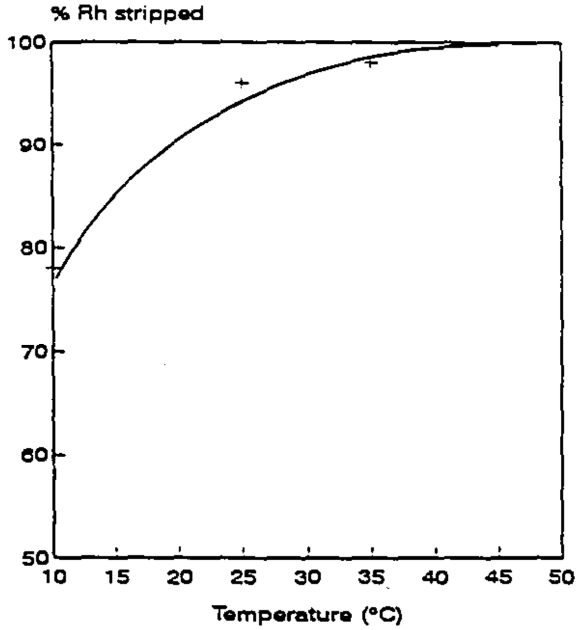
The effect of acidity was also studied in the lower acid region, since earlier studies had shown that for a 0.5M Na_2SO_3 solution, stripping increased with increasing HCl concentration, in the lower acid region (see Figure 5.8). This behaviour is unexpected from the standpoint of reaction 5.7, since protons are released during stripping. In the region tested (0,1 - 2.0 H^+), thermodynamics predict no SO_3^{2-} and the effect of acidity is therefore not related to the relative SO_3^{2-}/HSO_3^- distribution. In addition, since the stripping reaction involves the breaking of an ion-pair, it is expected that lower acidities would be preferred. The reason for the increase in stripping efficiency with increasing acidity, up to about 2.5M HCl is not known.

The equilibrium stripping constant was calculated using equation 5.8 and a value of log $K_{Rh,S} = 3.1 \pm 0.2$ was obtained. Although the stripping reaction constant is significantly lower than the extraction constant, it is still sufficiently large for rhodium stripping to be readily achieved. This is shown further in the stripping isotherm below.

Tests were performed to evaluate the effect of temperature on rhodium stripping. The stripping of rhodium as a function of temperature is displayed in Figure 5.15. From this Figure, it can be seen that stripping increases with increasing temperature, the usual trend for stripping reactions. It is possible to evaluate the enthalpy change, ΔH°, for rhodium stripping. Since all of the parameters were kept constant, the enthalpy can be calculated as follows by using the Van't Hoff equation

$$\text{Log } K_{Rh,S} \propto \text{Log } D_{Rh,S} = -\Delta H^\circ / 2.3RT + \text{const.} \qquad (5.9)$$

The Van't Hoff plot is shown in Figure 5.16. An enthalpy change of 87kJ/mol was determined, i.e., the stripping reaction is endothermic.



8.0×10^{-3}M Rh in organic, O/A=1, CT=20 minutes, 0.058M Kelex 100

Figure 5.15: Effect of temperature on rhodium stripping with 2.4M HCl and 0.5M Na_2SO_3.

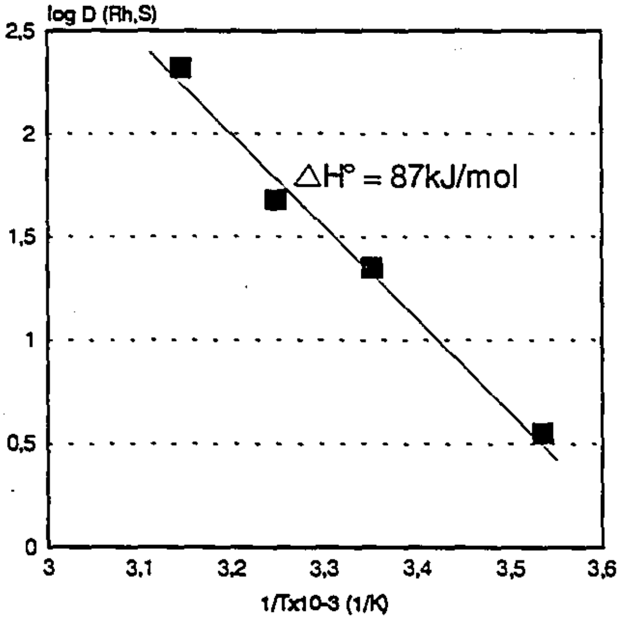
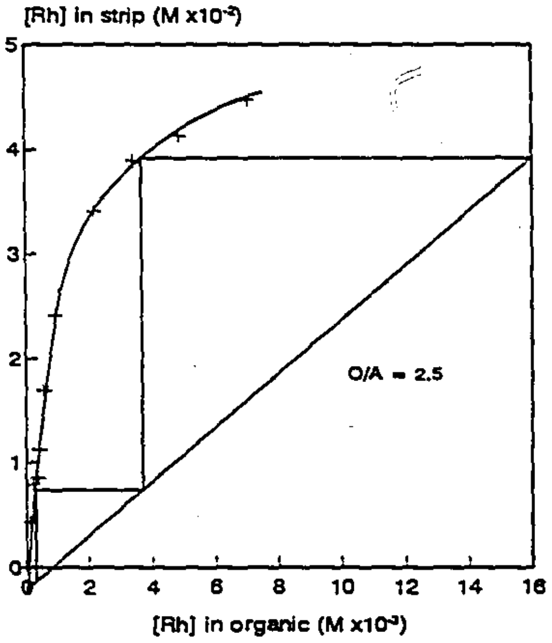


Figure 5.16: Van't Hoff plot for the rhodium stripping reaction.

With the aim of designing an industrial process, it is important to obtain the stripping isotherm and McCabe-Thiele diagram. These are shown in Figure 5.17 for a 0.058M Kelex 100 solution. Similarly to the extraction isotherm, the stripping isotherm has a sharp initial rise which represents very high distribution coefficients for stripping, even from barely loaded organics. The isotherm then rises more gradually, and no plateau is found although some curvature is evident.

Figure 5.17 can be used to calculate the number of theoretical counter-current stripping stages required for a given organic at a specified O/A ratio. Assuming that the loaded organic contains 1.6x10^{-2}M Rh, if an organic to aqueous ratio of two and a half is used, then only two contacts are sufficient to achieve a strip solution containing 4.0x10^{-2}M Rh and a stripped organic containing less than 20 ppm rhodium.



1.2x10-2M Rh in organic, 3:1 Sn:Rh, CT=20 minutes

Figure 5.17: McCabe-Thiele diagram for rhodium stripping from 0.058M Kelex 100 solutions.

5.5 FLOWSHEET REFINEMENTS

5.5.1 Tin Scrubbing

At the end of the stripping stage, most of the tin is still in the organic, most likely as $SnCl_3 \cdot H_2Q$, and this tin must be removed before the next cycle, if the rhodium loading level is to remain high. An interesting idea, however, was that it might be possible to keep the tin in the organic and use this tin to "activate" a pure rhodium chloride solution. This would have as beneficial effect to severely lower the amount of tin required to run the solvent extraction circuit. Such a test was carried out by contacting a Sn(II)-loaded organic with a pure solution of rhodium chloride, both at room temperature and at 70°C, for a contact time of two hours. Unfortunately, extraction levels comparable to those of pure rhodium chloride solutions were obtained, i.e., only $[RhCl_6]^{3-}$ appears to be extracted and activation does not occur. The tin must therefore be removed from the organic. Similarly to the system described in Chapter 4, the tin can be scrubbed using a 1M NaOH solution for a contact time of one hour. The organic is then reconditioned by contacting it with an acidic solution, and it is then ready to be recycled back to the extraction stage. Scrubbing efficiency tests for the NaOH solution were not performed and therefore quantitative data cannot be presented. Recycling of the tin was not investigated as part of this work but it should be investigated in the event that this system finds industrial application.

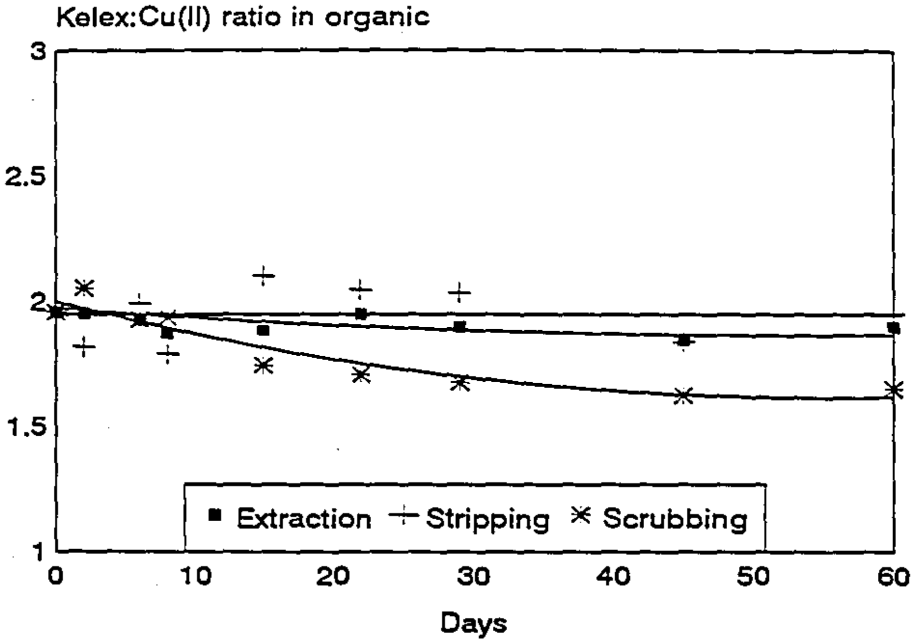
5.5.2 Recycling

A number of complete solvent extraction cycles were performed to ensure that the behaviour of the organic would remain unchanged over a number of cycles. Quantitative extraction and stripping was found for three consecutive cycles, with 8×10^{-3}M Rh feed solutions and intermediate tin scrubbing. Although this test is very limited in terms of the number of recycles, it serves to show that there is no immediate problem and that a more substantial recycling investigation could be carried out if the system were to be investigated further.

5.5.3 Organic Degradation

The organic was also tested for degradation over time. This test was performed by keeping, in closed vessels, organic solutions in continuous contact, over sixty days, with aqueous solutions of (i) 1.5M HCl + 1.5M $MgCl_2$, to simulate the feed solution, (ii) 2.4M HCl + 0.5M Na_2SO_3, to simulate the strip solution, and (iii) 1M NaOH, to simulate the tin scrub solution. The organic was regularly sampled and quantitatively loaded with Cu, a standard procedure to determine the degradation of Kelex 100 [11]. The copper loading results are shown in Figure 5.19. It was found that the organic responds well to these three solutions with insignificant degradation, over sixty days.

The very low degradation of Kelex 100 with the NaOH solution could come as a surprise since it is known that Kelex suffers from a limited resistance to oxidation when in contact with caustic solutions. One factor which may have limited the degradation is that there was little air present since the contact was peformed in a closed system. More important, however, may be that 1M NaOH solutions have been found to be much less harmful to Kelex 100 than even 1.5M solutions [11]. Given that for the system designed here a one hour contact with a 1M NaOH solution is sufficient for tin scrubbing, no special precautions need be taken against caustic oxidative degradation. It should also be kept in mind that the system is for rhodium, one of the precious group metals, and some minor cost considerations may not be as important as for the lower value elements.



2v% Kelex 100, 10v% tridecanol, Cu(II) loading at pH4.0

Figure 5.18: Degradation of the 0.058 Kelex 100 organic solution over time when kept in contact with various aqueous solutions.

5.5.4 Selectivity and Rhodium Recovery

One of the main objectives of a solvent extraction ciruit is to purify a given species or element and selectivity is therefore a most important characteristic. In this case, a foreign element, tin, is introduced and it is important to carefully track it's behaviour throughout the system. So far, it has been reported that tin is quantitatively co-extracted with rhodium, as part of $[RhCl_3(SnCl_3)_3]^{3-}$, and that it does not report, in significant quantities, in the rhodium strip solution.

Stripping/scrubbing of tin is more quantitatively defined here. In fact, it was generally found that about 100 ppm of tin does get back-extracted during the rhodium stripping stage, when using the typical strip solution (0.5M Na_2SO_3 in 2.4M

HCl) and the typical rhodium and tin loading level in the 2v% Kelex 100 solution (about 4×10^{-3}M rhodium and $1,2\times10^{-2}$M tin). Considering the tin loading level, it might seem that 100 ppm is not all that much, however, since the final rhodium metal purity aimed for is 99.95% Rh, it becomes important to devise a rhodium recovery step that is selective over tin.

One important note here is that it was found that high concentrations of tin in the sulfite strip solution cause this solution to become unstable. When high levels of tin are co-stripped during rhodium stripping, a yellow precipitate is slowly formed in the strip solution. To investigate the formation of this precipitate, 0.1M $SnCl_2$ was dissolved directly into a 0.5M Na_2SO_3 in 2.4M HCl solution. Although the salt immediately quantitatively dissolved, a colloidal like suspension started to form after about fifteen minutes and a yellow precipitate was obtained after about one hour. The precipitate was not analyzed, however, its yellow color could lead to the suspicion that a sulfur product is formed. A possible redox reaction between the stannous species and the sulfite sulfur could occur as follows:

$$2SnCl_3^- + SO_3^{2-} + 6Cl^- + 6H^+ \rightarrow S^\circ + 2SnCl_6^{2-} + 3H2O \qquad (5.10)$$

The standard potentials of the H_2SO_3/S° couple (0.449V) and the Sn^{4+}/Sn^{2+} couple (0.151V) are such that the above reaction would be thermodynamically possible.

A similar test was performed with 0.05M $RhCl_3$ salt, however in this case no precipitate was noticed.

At the end of the solvent extraction circuit, rhodium must be recovered from the strip solution. Only limited experimental work was done in this regard. First, because there is very little Sn(II) in the strip solution, rhodium cannot be recovered directly through simple in-situ Sn-Rh redox precipitation caused by heating, as for the previous system (Chapter 4.4.3). In addition, since there is some tin present, the rhodium must also be recovered selectively against tin. Recovering the rhodium through reduction with SO_2 gas would have been elegant, as it would also have been a method of maintaining a very potent strip solution. Unfortunately, the reaction does not proceed, at least under the conditions tested here (2.2 atm SO_2 (g) and 2.4M HCl, 25°C, two hours). It is possible to recover rhodium through hydrogen reduction, however. Quantitative rhodium precipitation was found when a typical strip solution was treated at 3.4 atm H_2 at 50°C for two hours. This method, though slightly more complicated than that of the previous system is nonetheless also quite advantageous, when compared to other common reducing techniques such as formic acid or oxalic acid reduction. No foreign substances are introduced, ensuring that the strip solution can be reused after rhodium recovery. Also, the reducing atmosphere ensures that the sulfite is not converted to sulfate during rhodium reduction. Tin was found to be inert to hydrogen reduction and therefore selectivity appears to be feasible. Simple atomic absorption analyses indicate that the back-extracted tin in the strip solution does not contaminate the rhodium powder obtained, but an analysis of the precipitate itself must be performed before its true purity can be established.

One possible problem with hydrogen reduction, however, is that a very small amount of yellow sulfur was found to have deposited on the ceiling of the reactor. Pure solutions of sodium sulfite in 2.4M hydrochloric acid proved to be inert to H_2 reduction, under the same conditions, even though thermodynamically, the reduction should occur ($e_{H+/H2}$=0.007V for H^+/H_2 and e_{H2SO3/S°=0.47V for H_2SO_3/S° for 0.5M Na_2SO_3 in 2.4M HCl with 3.4 atm H_2 at 50°C). It is likely that the sulfur is due only to the reduction of the sulfite ligands in the rhodium strip complex and not to a bulk reduction of sulfite in hydrochloride acid. Alternatively, the sulfite reduction might be due to a catalytic effect of rhodium metal, or it could be caused by the small amount of tin present as postulated in equation 5.10. To limit the amount of sulfur produced, it would be important to perform a kinetic-selectivity investigation on the reduction of rhodium from the strip solution with H_2 (g).

5.6 CONCEPTUAL SOLVENT EXTRACTION PROCESS FLOWSHEET

A simplified flowsheet of the solvent extraction process is presented in Figure 5.20. It is based on a $4x10^{-3}$M Rh solution and a 0.058M Kelex 100 organic solution. Activation is carried out first with a Sn(II):Rh ratio of about 3:1 for about fifteen minutes at 70°C (this procedure has not been optimized and it appears that shorter time or lower temperatures would be sufficient). Once the activated feed has been cooled to room temperature, the organic is loaded to 0.016M rhodium by working at an A/O ratio of four and by performing two consecutive counter-current extractions. A raffinate of less than five ppm rhodium is obtained. The loaded organic then goes to stripping, with 0.5M Na_2SO_3 in 2.4M HCl, where two counter-current contacts are required, if an A/O ratio of two and a half is used, to produce a strip solution containing 0.040M rhodium and an organic containing less than 20 ppm rhodium. A total concentration ratio of ten is achieved in this way. The organic which has been stripped of rhodium must be scrubbed of tin. This can be achieved with a one hour contact of 1M NaOH. The organic should then be contacted with an acidic solution, for example 2M HCl for two minutes, and then it is ready to return to the extraction stage. It need not be deacidified with water washes. The strip solution can be heated in an autoclave at 50°C under 3.4 atm H_2(g) pressure for two hours and fine, black rhodium-containing powder is obtained.

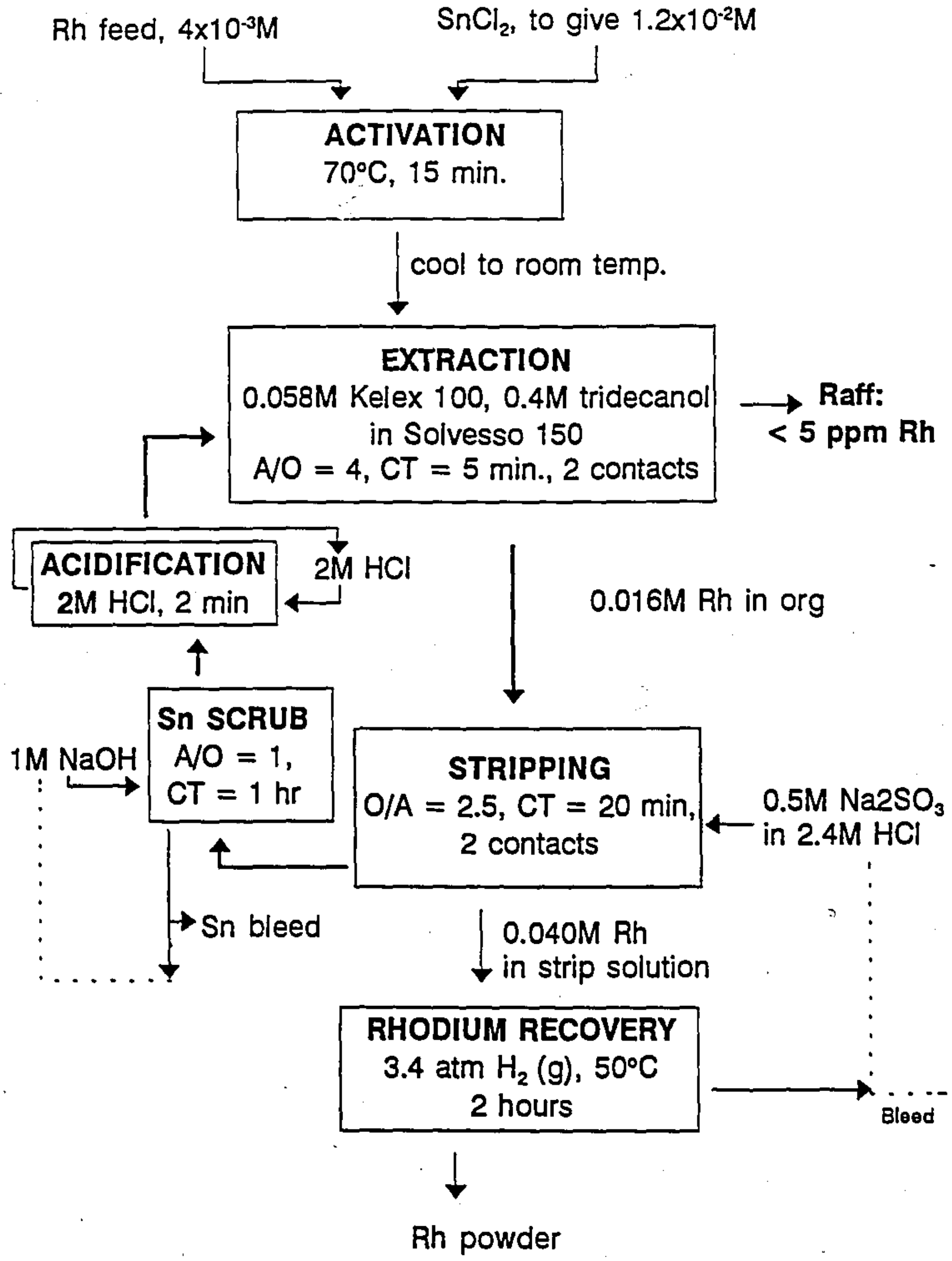


Figure 5.19: Simplified flowsheet of the solvent extraction system for a dilute rhodium feed (400 ppm) based on 3:1 Sn(II):Rh activation, with Kelex 100 (2 v%), 0.5M Na_2SO_3 in 2.4M HCl as strip solution, 1.0M NaOH as tin scrub solution, and H_2 reduction for rhodium recovery.

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CHAPTER 6

THE LOW Sn:Rh (<6:1) SYSTEM: STRIPPING KINETICS

6.1 INTRODUCTION

In this Chapter, the kinetics of the sulfite stripping stage are described. The stripping stage is the most complicated, since in contrast to conventional stripping systems, it involves a complex chemical reaction with initial reactants in two different phases. Also, the rhodium stripping product does not appear to have yet been described in the literature. To better understand this stage, and the mechanism by which the stripping reaction occurs, a kinetic investigation was undertaken. Special equipment, described in Chapter 3, was required for this study such the the interfacial area could be controlled through the use of an organic-permeable membrane. Very few studies have been undertaken in the past on examining the stripping stage kinetics in solvent extraction systems, with most of the studies focusing uniquely on the extraction stage. In the family of PGM solvent extraction systems, only one study so far has mentioned stripping kinetics, notably the stripping kinetics of Pd from alkylated 8-hydroxyquinoline (similar to Kelex 100) [1].

6.2 KINETIC RESULTS

The stripping reaction for the solvent extraction system described in Chapter 5 has been described as:

$$\overline{[RhCl_3(SnCl_3)_3\cdot(H_2Q)_3]} + 2HSO_3^- - [RhCl_2(SO_3)_2]^{3-} + 2H^+ + Cl^- + 3\overline{[SnCl_3\cdot H_2Q]} \quad (6.1)$$

The stoichiometry of the above reaction is based on the slope analysis study presented in the previous Chapter (see section 5.4.3). Reaction 6.1 is believed to be irreversible since it was found that no rhodium was extracted when a 8x10^{-3}M rhodium-containing sulfite strip solution (0.5M Na_2SO_3 in 2.4M HCl) was contacted with a 0.058M Kelex 100 organic solution. For the kinetic tests, the 0.058M Kelex 100 organic solution was loaded to about 75% of its maximum loading level (0.015M Rh) and the stripping reaction was allowed to proceed until about 50% completion. The parameters investigated for the kinetic study were stirring speed, sodium sulfite concentration (0.15 - 0.5M Na_2SO_3), acidity (2.4 - 4.2M H^+), chloride ion concentration (2.4 - 4.2 Cl^-) , free Kelex 100 concentration (0.014 - 0.188M), and isodecanol concentration (0.41-1,63M). Each of the variables was examined separately with all other conditions kept constant while the temperature was fixed at 25±1°C, through the use of a water bath.

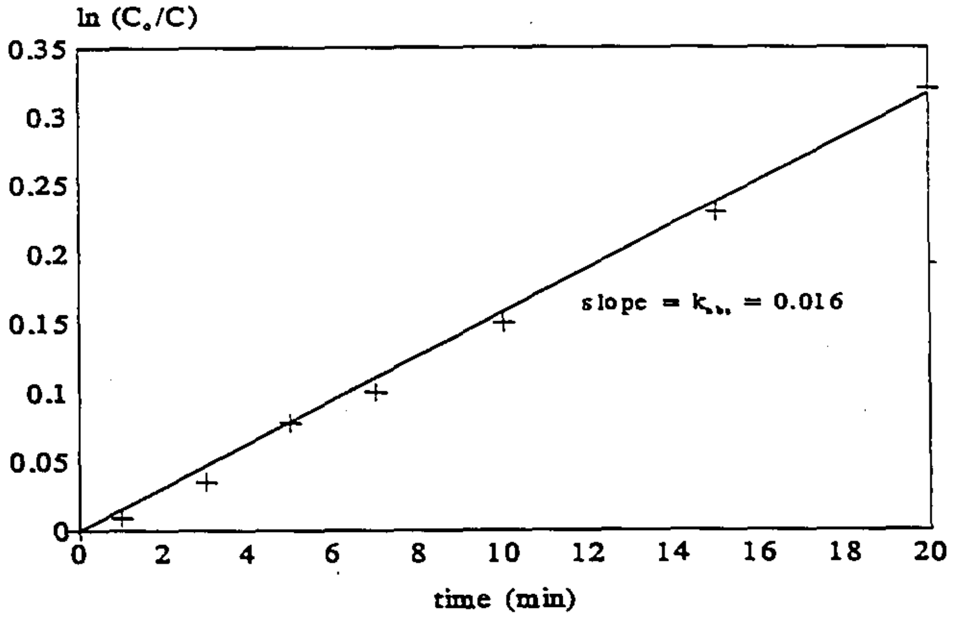
6.2.1 Method of Data Analysis

The method of integration, rather than initial rates was used to analyze the kinetic tests. It has been suggested that the "method of fitting integral kinetic data, preferably measured up to practical equilibrium, by calculated curves obtained by integration of the rate equation, is generally more reliable than the method of initial rates" [2].

Because the stripping reaction is believed to be irreversible, and since the organic is highly loaded and the rates are determined from the first half of the reaction, the observed reaction constants are assumed to be for the forward reaction only. The pseudo-first order rate constants, k_{obs}, were determined from

$$\ln (C_o/C_t) = k_{obs}t \qquad (6.2)$$

where C_o and C_t correspond to the concentration of rhodium in the organic at time zero and at time t, respectively. A typical first-order plot is shown in Figure 6.1.



0.3M Na_2SO_3 in 2.4M HCl

Figure 6.1: First order integration plot for rhodium stripping with 0.3M Na_2SO_3 in 2.4M HCl.

To calculate the reaction order with respect to any of the components, other than $[Rh]_{org}$, the log k_{obs} values are plotted against the log of the concentration of the component, according to the following rate equation:

$$r_{Rh} = k_{obs}[Rh_{org}]^a[SO_3^{2-}]^b[Cl^-]^c... \qquad (6.3)$$

It was verified that the stripping reaction is, in fact, first order in terms of rhodium by varying the initial concentration of rhodium in the loaded organic, while maintaining the loading degree at 75%, and by calculating the order of the reaction through the following equation derived from equation 6.3:

$$\log r_{Rh} = \log k_{obs} + a \log [Rh_{org}] + b \log [SO_3^{2-}] + c \log [Cl^-] ... \quad (6.4)$$

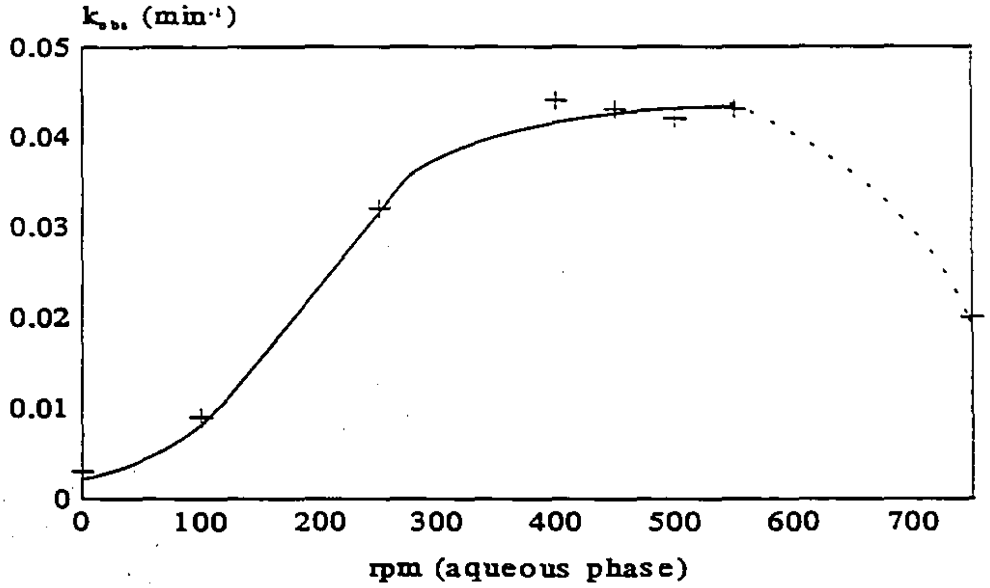
The results obtained are given in Table 6.1 and when the logs are taken according to equation 6.4, it is clear that the reaction is in fact first order in terms of rhodium (a=1.05 and r^2=0.99), no matter if the integration or differential method is used.

Table 6.1: Results of rhodium reaction order using differential technique.

C_o (Mx10^{-2})	r_{Rh} (d[Rh]/dt) (M/min^{-1})
1.90	75.2
1.22	51.7
0.63	24.2
0.44	16.3

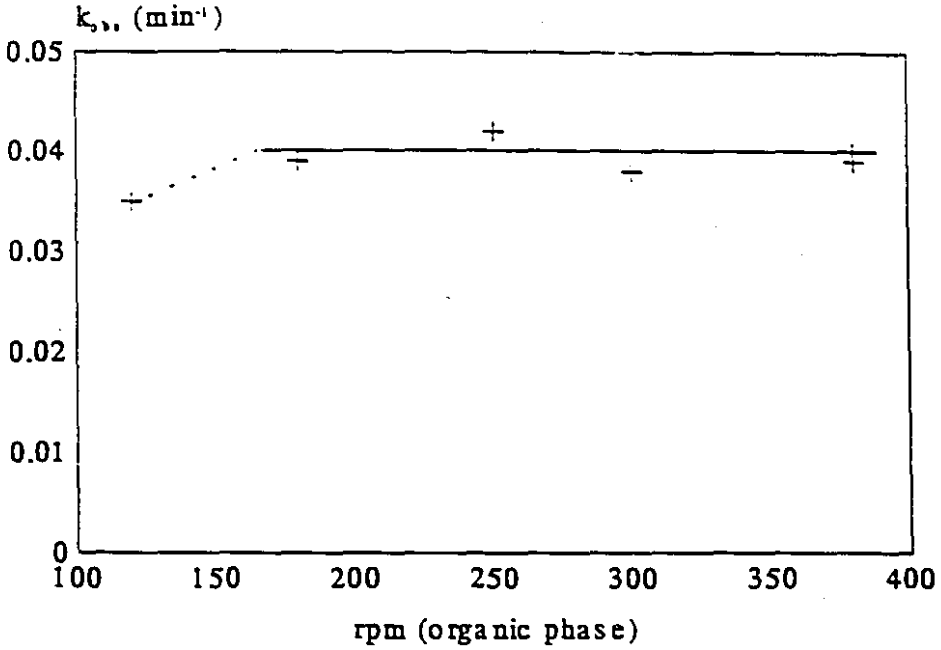
6.2.2 Stirring Speed

The stirring speed was altered for both the aqueous and the organic phases, separately, since these are stirred independently as shown in Figure 3.1. Figures 6.2 and 6.3 show the observed reaction rate constants, k_{obs}, obtained by varying the stirring speeds for the aqueous and organic phases, respectively, while maintaining all other conditions constant (0.5M Na_2SO_3, 2.4M HCl, 0.015M Rh_{org}). Discussing first the aqueous stirring speed effect, it can be noticed that the observed rate constant increases with increasing stirring speed, reaches a plateau, from about 400 rpm to 550 rpm, and then actually decreases again at the highest speed tested, 750 rpm. The decrease would be rather unusual, but it can be explained in this case. At such high stirring speeds, a vortex was found to occur in the aqueous solution and a part of the membrane, which is equivalent to the interface, was no longer in contact with the aqueous solution. The reduction in effective interfacial area is actually the cause of the reduced observed reaction constant. An aqueous stirring speed of 500 rpm was chosen for further tests as it lied on the plateau region where no vortex was observed. The organic stirring rate was found to have less influence in the plateau region tested, from about 175 rpm to about 400 rpm. A stirring speed of 200 rpm was chosen for all further tests.



after 30 minutes contact time
organic: 200 rpm, 0.058M Kelex 100 loaded with 0.015M Rh
aqueous: 0.5M Na2SO3 in 2.4M HCl

Figure 6.2: Effect of aqueous stirring speed on observed reaction constant.



after 30 minutes contact time
organic: 0.058M Kelex 100 loaded with 0.015M Rh
aqueous: 500 rpm, 0.5M Na_2SO_3 in 2.4M HCl

Figure 6.3: Effect of organic stirring speed on observed reaction constant.

Discussing now the implications of the observed stirring speed effects, it can be said that choosing to work in the plateau region does not necessarily indicate that the system is controlled by the rate of the interfacial chemical reaction only, but it could be that diffusion through the limiting boundary layer is the rate limiting step [3]. But given that the stripping reaction is not the simple reversal of the extraction reaction but involves the formation of totally new chemical complexes, it will lead to the assumption that the rate limiting step is the reaction itself, i.e., the formation of $RhCl_2(SO_3)_2^{3-}$. In addition, since the overall interfacial area was not changed, it is not possible with absolute certainty to designate the locus of the rate controlling chemical reaction, i.e. at the interface, or inside the nearby aqueous or organic diffusion layers. The one test where the interfacial area was inadvertently decreased due to vortex formation, might point to an interfacial reaction, since the observed reaction rate was significantly decreased, however in this case, the total area of the aqueous liquid boundary layer was also decreased therefore no conclusion can be reached. It should be pointed out, also, that Kelex 100 is not very soluble at all in the aqueous phase, having a partition coefficient of 3.31×10^5 [4] and this might lead to thinking that it is more likely that the reaction will occur at the interface.

6.2.3 Reaction Orders

The reaction order, in terms of the various reactants and products of reaction 6.1 were obtained next. For sodium sulfite, the concentration was varied from 0.15 to 0.5M while the acidity was fixed at 2.4M HCl. The observed rate constants, k_{obs} (slopes of the first order plots), for the various sodium sulfite concentrations are given in Table 6.2.

Table 6.2: Observed rate constants as a function of sodium sulfite concentration in 2.4M HCl.

Na_2SO_3 conc'n, M	k_{obs} (min^{-1})
0.15	0.004
0.22	0.008
0.30	0.016
0.40	0.024
0.5	0.044

To obtain the reaction order with respect to sodium sulfite, a plot of the log of the observed rate constants versus the log of the sodium sulfite concentration was produced and is shown in Figure 6.4. The reaction order for sodium sulfite was found to be 1.95 ($r^2 = 0.994$).

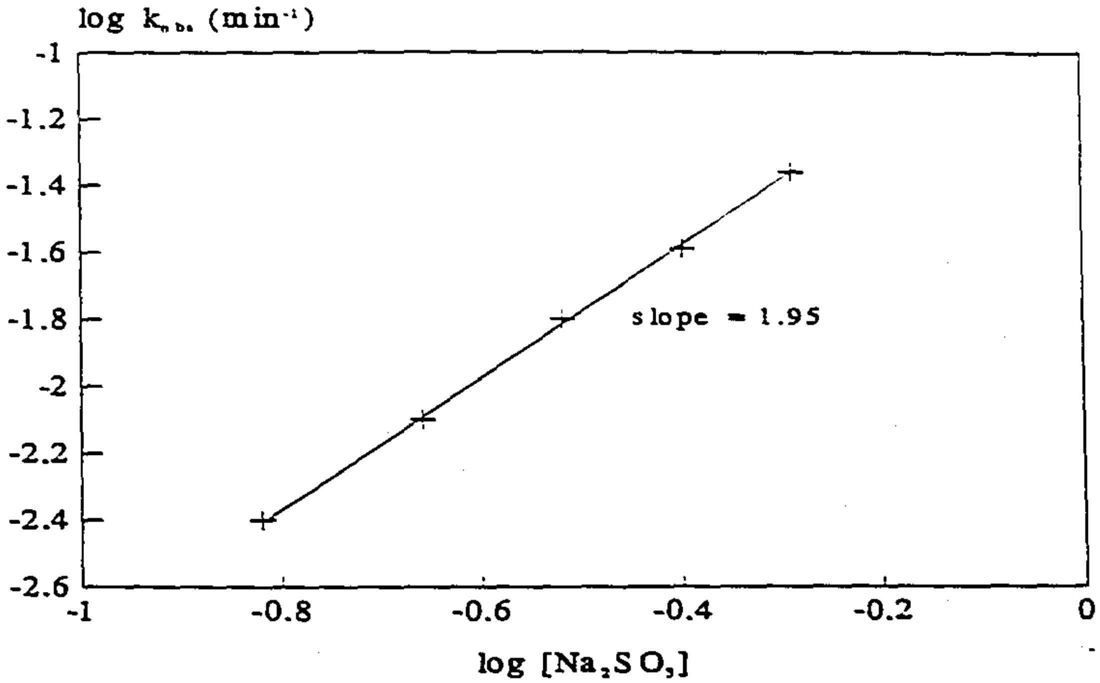


Figure 6.4: Log-log plot of the observed reaction rate constant versus the Na_2SO_3 concentration in 2.4M HCl.

Similar tests were performed for proton and chloride ion concentration. The proton concentration was varied through the addition of various amounts of HCl, while maintaining the total chloride concentration at 4.2M through the addition of $MgCl_2$. Similarly, the total chloride ion concentration was varied by adding different amounts of $MgCl_2$ to a solution containing 2.4M HCl. The observed rate constants are listed in Tables 6.3 and 6.4 and the reaction order plots are shown in Figure 6.5 and 6.6, for proton and chloride ion concentration, respectively. Reaction orders of -1.7 ($r^2 = 0.990$) for acidity and -1.8 ($r^2 = 0.990$) for chloride ion were obtained.

Table 6.3: Observed rate constants as a function of proton concentration for 0.5M Na_2SO_3 and 4.2M Cl^- solutions.

H^+ conc'n, M	k_{obs} (min^{-1})
1.9	0.016
2.5	0.010
3.0	0.008
3.7	0.005

Table 6.4: Observed rate constants as a function of chloride ion concentration for 0.5M Na_2SO_3 and 2.4M H^+ solutions.

Cl^- conc'n, M	k_{obs} (min^{-1})
2.4	0.044
3.0	0.027
3.5	0.021
4.2	0.016

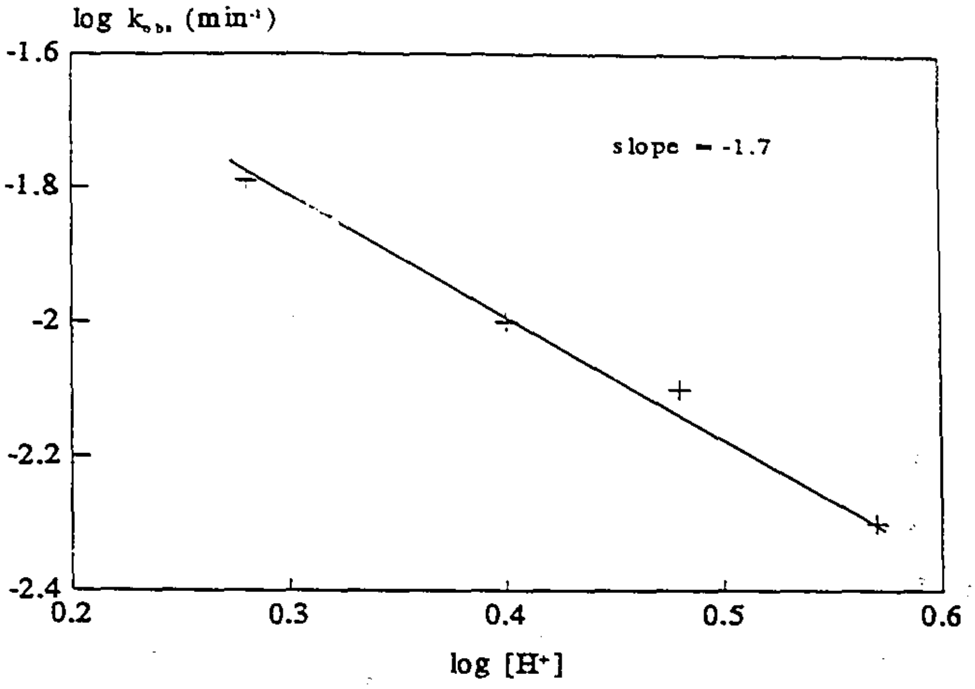


Figure 6.5: Log-log plot of the observed reaction rate constant versus proton concentration with 0.5M Na_2SO_3 and 2.4M Cl^-.

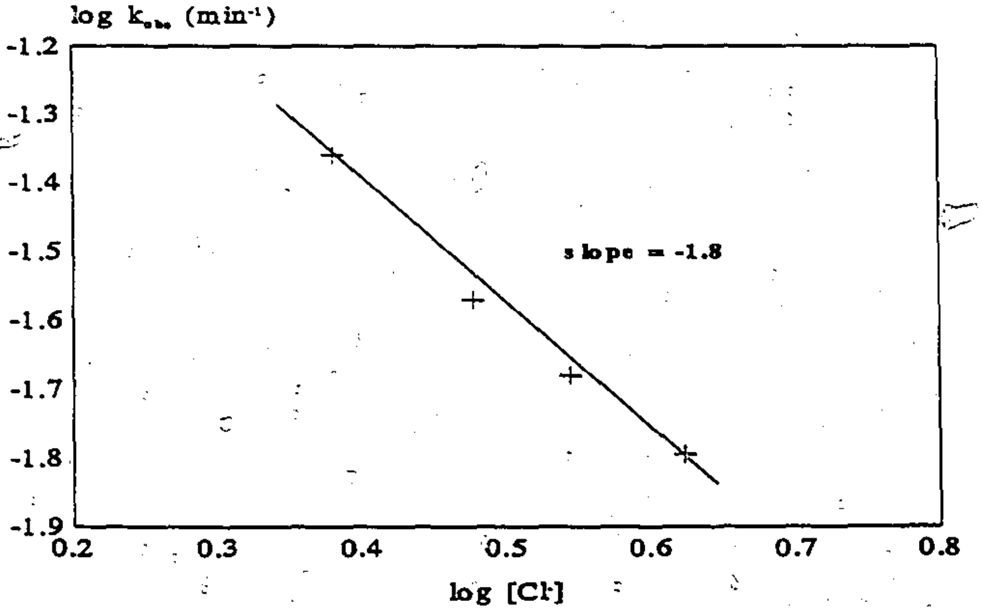


Figure 6.6: Log-log plot of the observed reaction rate constant versus the chloride ion concentration with 0.5M Na_2SO_3 and 2.4M H^+.

The effect of free Kelex 100 concentration on the rate was also investigated but here the results are not as clear. If the reaction is irreversible, then the free Kelex 100 concentration, or more precisely, the free protonated Kelex 100 concentration, should have no effect on the rate. On the other hand, one of the reaction products, $SnCl_3 \cdot H_2Q$ does involve the extractant. There are also two methods of varying the Kelex 100 concentration. One is by simply increasing the concentration while maintaining the tridecanol concentration constant (at 0.41M), and the other is by increasing the Kelex 100 concentration while simultaneously increasing the tridecanol concentration such that the total extractant to modifier volume ratio is maintained (at 5:1 modifier to extractant). Both of these methods were attempted and the results are shown in Figure 6.7. Without yet trying to explain the effect of the modifier on Rh stripping, it is clear that for both curves in Figure 6.7, higher free protonated Kelex concentrations noticeably lower the kinetics of the stripping reaction. One possible explanation may be that the free protonated Kelex molecules crowd the interface, blocking access to Rh-loaded Kelex molecules. In addition, since the two curves are not identical, it appears that tridecanol is not indifferent but in some way interacts with the extractant, facilitating (to a certain degree) the interfacial mass transport process. The interaction might very well involve formation of water in oil (W/O) microemulsions wherein protonated Kelex and tridecanol molecules participate [5].

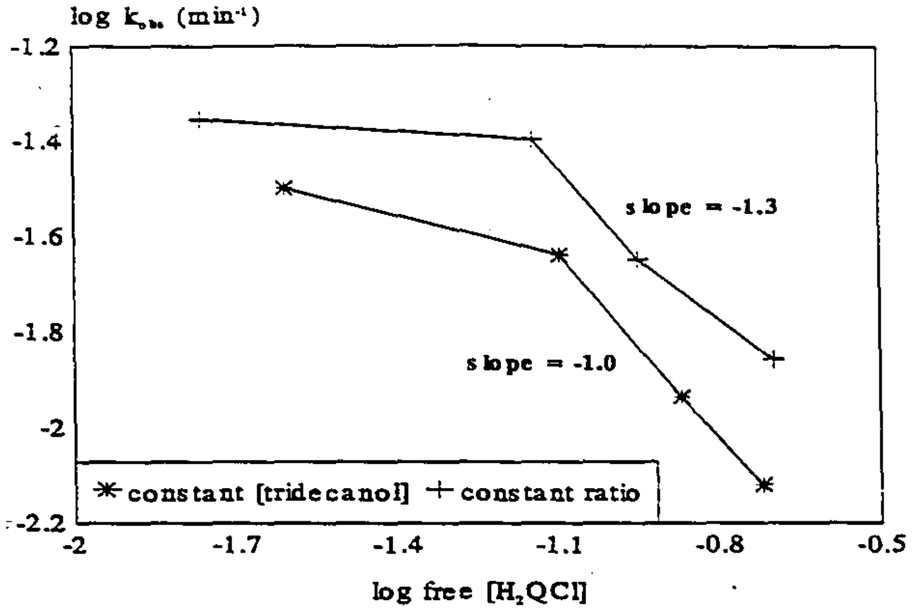


Figure 6.7: Log-log plot of the observed reaction rate constant versus the Kelex 100 concentration with 0.5M Na_2SO_3 in 2.4M HCl.

6.3 STRIPPING MECHANISM

The stripping mechanism must be quite complex as the reaction involves reactants initially present in two different phases and at least four bonds breaking due to ligand substitution, not to mention the possible involvement of redox coupling. In addition, the complex order dependence of the stripping reaction, -2 for chloride and hydrogen ion, -1 for free protonated Kelex 100, +2 for sulfite,+1 for rhodium and -2 for $SnCl_3^-$ (this not determined but assumed), is such that it is probably not possible, with the limited information available here, to postulate an accurate reaction mechanism. In fact, more complete tests on the effects of solubility, ligand strengths and redox properties of the formed complexes should be performed to have a better understanding of the reaction mechanism. Nevertheless, for completeness, a simplified reaction mechanism is proposed here which in appearance fits the experimental kinetic stoichiometries. It is realized that the proposed path may prove to be inaccurate under closer scrutiny.

$$[RhCl_3(SnCl_3)_3^{3-}\cdot(H_2Q^+)_3]_{(org)} \overset{K_4}{\rightleftharpoons} [RhCl_3(SnCl_3)_3^{3-}\cdot(H_2Q^+)_3]_{(i)} \qquad (6.5)$$

$$[RhCl_3(SnCl_3)_3^{3-}\cdot(H_2Q^+)_3]_{(i)} \overset{K_5}{\rightleftharpoons} [RhCl_3(SnCl_3)_3^{3-}] + 3H_2Q^+_{(i)} \qquad (6.6)$$

$$[RhCl_3(SnCl_3)_3]^{3-} + HSO_3^- \overset{K_6}{\rightleftharpoons} [RhCl_3(SnCl_3)(SO_3)]^{3-} + 2SnCl_3^- + H^+ \qquad (6.7)$$

$$SnCl_3^- + H_2Q^+_{(i)} \overset{K_7}{\rightleftharpoons} [SnCl_3^-\cdot H_2Q^+]_{(org)} \qquad (6.8)$$

$$[RhCl_3(SnCl_3)(SO_3)]^{3-} + HSO_3^- \overset{K_8}{\rightleftharpoons} [RhCl(SnCl_3)(SO_3)_2]^{3-} + 2Cl^- + H^+ \qquad (6.9)$$

$$[RhCl(SnCl_3)(SO_3)_2]^{3-} \overset{k_9}{\rightarrow} [RhCl(SO_3)_2]^{2-} + SnCl_3^- \qquad \text{r.d.s} \qquad (6.10)$$

$$[RhCl(SO_3)_2]^{3-} + Cl^- \rightarrow [RhCl_2(SO_3)_2]^{3-} \qquad (6.11)$$

$$r=k_9K_5K_6K_7K_8[RhCl_3(SnCl_3)_3\cdot(H_2Q)_3][HSO_3^-]^2 - [Cl^-]^{-2}[H^+]^{-2}[H_2Q^+]^{-1}[SnCl_3\cdot H_2Q]^{-2} \qquad (6.12)$$

The reaction mechanism proposed above begins with the distribution of the rhodium complex at the aqueous/organic interface. The reaction is assumed to proceed relatively readily with the addition (association) of the sulfite ligands and the slow departure (exchange) of the third $SnCl_3^-$ ligand (r.d.s equation 6.10). Although octahedral complexes generally undergo ligand substitution reactions via dissociative mechanisms [6], it is not necessary that it be the departure of a ligand rather than the association of a ligand that be the rate determining step. Here, the reaction scheme proposed above is given only as an example of a path which "fits" the experimental reaction orders.

6.4 REFERENCES

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CHAPTER 7
SUMMARY

7.1 CONCLUSIONS

The intent of this research project was to study the chemistry of the Rh(III)-HCl-$SnCl_2$-Kelex 100 solvent extraction system from the standpoint of assessing it for potential use for the refining-recovery of rhodium from chloride-based industrial solutions. Two variants of this novel solvent extraction system were developed. The first of these (Chapter 4) involved a Sn:Rh ratio higher than 6:1 and stripping of the loaded organic with sulfuric acid. The second (Chapters 5 and 6) involved a Sn:Rh ratio of less than 6:1 and stripping of the loaded organic with sodium sulfite in hydrochloric acid. For both systems, rhodium can be quantitatively extracted from aged Rh(III) chloride solutions and transferred into aqueous strip solutions - this being the first time achieved with commercially available solvent extraction reagents. The critical part for both systems is their stripping stage. It appears to be difficult to obtain concentrated strip liquors, with this being more pronounced for the high Sn:Rh system. The low Sn:Rh system appears to offer most promise for application to extraction and concentration of rhodium from dilute (about 5×10^{-3}M) solutions. The major findings of this work are enumerated below. Since this work is divided into two main sections, the high and low tin systems, the conclusions presented here will also be divided in two sub-sections.

7.1.1 The high Sn:Rh (>6:1) system

1. The only detectable complex in the 12:1 Sn(II):Rh activated aqueous solution is $[Rh(SnCl_3)_5]^{4-}$.

2. $[Rh(SnCl_3)_5]^{4-}$ can be quantitatively extracted within five minutes through ion-pair formation, with protonated Kelex 100, such that the extracted complex can be described as $[Rh(SnCl_3)_5 \bullet (H_2Q)_4]$.

3. For a 0.058M Kelex 100 solution, up to 0.015M Rh can be loaded in the organic phase.

4. Stripping can be achieved with sulfuric acid solutions. The one chosen for this work is 1.7M H_2SO_4 + 1M Na_2SO_4.

5. The loading level of the organic has a strong influence on the amount of rhodium that can be stripped from the loaded organic phase, with increased loading showing increased overall stripping.

6. The presence of chloride ion in the organic phase inhibits the stripping of rhodium from the loaded organic into the sulfuric acid strip solution.

7. Concentrated strip solutions ($>3\times10^{-3}$M) cannot be achieved, because of the low distribution coefficient of the rhodium strip complex between sulfuric acid and the Kelex 100 organic solution, and because of the low solubility of the stripped rhodium complex in sulfuric acid.

7.1.2 The low Sn:Rh (<6:1) system

1. At a 3:1 Sn(II):Rh ratio, the complex $[RhCl_3(SnCl_3)_3]^{3-}$ appears to be the dominant complex in the HCl aqueous solution, according to ^{119}Sn NMR.

2. $[RhCl_3(SnCl_3)_3]^{3-}$ is quantitatively extracted within five minutes through ion-pair formation, with protonated Kelex 100, such that the extracted complex can be described as $[RhCl_3(SnCl_3)_3 \cdot (H_2Q)_3]$.

3. For a 0.058M Kelex 100 solution, up to almost 0.02M Rh can be loaded in the organic phase.

4. Stripping can be achieved with acidic solutions of sodium sulfite. The one chosen in this work is 0.5M Na_2SO_3 in 2.4M HCl.

5. The rhodium complex which can be stripped from the loaded organic with sodium sulfite is proposed to be $[RhCl_2(SO_3)_2]^{3-}$.

6. The stoichiometry and kinetics of the stripping reaction were studied.

7. Sodium sulfite strip solutions up to 4.5×10^{-2}M in rhodium were prepared from initial feeds of 4×10^{-3}M Rh using 0.058M Kelex 100.

7.2 CLAIMS TO ORIGINALITY

The work described in this thesis had as main objective process identification, and therefore, although many of the elements making up the work are not in themselves novel, the combination of them is. For example, solvent extraction of rhodium from chloride solutions with Kelex 100 had been briefly investigated by Benguerel et al [1], as had solvent extraction combined with $SnCl_2$ activation [2], but this is the only reported investigation of the solvent extraction of the Rh-Sn complexes with Kelex 100. The claims to originality listed below are proposed in this frame of consideration.

1. The use of UV spectroscopy to identify, on a practical scale, the complete activation of the rhodium solution to $[Rh(SnCl_3)_5]^{4-}$ versus the mixed $[RhCl_{6-x}(SnCl_3)_x]^{3-}$ is suggested for the first time in this work.

2. The use of Kelex 100 as extractant for the various Rh-Sn complexes is new and had never been reported in the literature.

3. The ^{119}Sn NMR and Raman spectra of both $[RhCl_{6-x}(SnCl_3)_x]^{3-}$ and $[Rh(SnCl_3)_5]^{4-}$ in the Kelex 100 organic phases had never been reported.

4. The identification of possible stripping solutions for the loaded Kelex 100 solutions is novel, as no previous work had ever been undertaken in this area.

5. The rhodium sulfite complex, $[RhCl_2(SO_3)_3]^{3-}$, proposed as existing in the sulfite strip solution is novel.

6. Most importantly, the two conceptual flowsheets for the solvent extraction of rhodium from chloride solution in the presence of stannous chloride with Kelex 100 are, in themselves, both contributions to original knowledge.

7.3 SUGGESTIONS FOR FURTHER INVESTIGATIONS

Because this work was followed quite closely by two industrial sponsors, there have already been some points which have been raised as requiring further investigation. Before these are listed, however, it should be mentioned that at this point, it is felt that no further work should be carried out on the high tin system, as the limitations in rhodium concentration in the strip solution preclude it from finding industrial applicability. For the low tin system, some of the work which might be pursued involves the following:

1. A study on the effect of impurity elements, including those belonging to the PGM group, on the activation, extraction and stripping behaviour of rhodium should be undertaken.

2. A study of the stripping stage, from the stand point of producing solutions having higher rhodium concentrations, including establishing the upper limits of rhodium stability.

3. The evaluation of other solvent extraction reagents having superior selectivity and stripping characteristics could be undertaken if this proves necessary..

4. Further work is required in connection with both the rhodium recovery (with H_2 or other reagents) and the tin scrubbing stages.

5. Finally, testing the preliminary flowsheet on a real industrial liquor, over a number of organic recycles would be appropriate at this point.

7.4 REFERENCES

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