Ion Flotation Studies and Separation Procedures for the Platinum Group Metals.

Daniel Murphy Downey

Louisiana State University and Agricultural & Mechanical College

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ION FLOTATION STUDIES AND SEPARATION PROCEDURES FOR THE PLATINUM GROUP METALS

The Louisiana State University and Agricultural and Mechanical Col. PH.D. 1980

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ION FLOTATION STUDIES
AND SEPARATION PROCEDURES
FOR THE PLATINUM GROUP METALS

A Dissertation

Submitted to the Graduate Faculty of the
Louisiana State University and
Agricultural and Mechanical College
in partial fulfillment of the
requirements for the degree of
Doctor of Philosophy

in

The Department of Chemistry

by

Daniel Murphy Downey
B.S., Madison College, 1975
May 1980
This work is dedicated to my wife, Carole, without whose patience and understanding it would not have been possible; and also to my mother, Charlotte, who could have used me on the farm.
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ABSTRACT

The purpose of this work was to study the ion flotation properties of the platinum group metals, develop methods for the quantitative recovery of the platinum metals from dilute solutions by ion flotation and investigate the feasibility of ion flotation for the group separation.

The anionic chlorocomplexes of Pd(II), Ir(IV), Pt(IV), Au(III), Rh(III) and Ir(III) were floated from aqueous solutions with cationic surfactants of the quaternary ammonium type, RNR’Br. The flotation behavior of each metal was determined with respect to variations of the surfactant primary, R, and secondary, R’, chain lengths, the initial HCl concentration, the initial NaCl concentration, the initial surfactant concentration and the initial metal chlorocomplex concentration.

Most of the surfactants prepared for this work floated the platinum metals; however, the maximum percentage of each metal floated varied significantly as the above parameters were varied. An increase in the percentage of all the metals floated was observed as the surfactant primary chain length was increased. As the surfactant secondary chain length was increased, the percentage of Au(III), Pd(II), Pt(IV) and Ir(IV) floated increased, but the percentage of Ir(III) and Rh(IV) floated significantly decreased. Furthermore, as the initial HCl or NaCl concentrations were increased, the percentage of each of the
metals floated decreased regardless of the surfactant used for flotation. The percentage of Ir(III) and Rh(III) floated decreased to zero as the initial HCl or NaCl concentration was increased to 0.5 M. The percentage of Pd(II) floated decreased to zero as the initial HCl concentration was increased to 2.0 M.

A general flotation selectivity sequence of Au(III) > Pd(II), Ir(IV), Pt(IV) > Ir(III) > Rh(III) was observed. Ion flotation enrichment ratios were calculated and compared to anion exchange distribution coefficients in order to verify the selectivity trends.

Optimum ion flotation conditions were established for the recovery of Au(III), Ir(IV) Pt(IV) and Pd(II) from dilute solutions. A modified solvent sublation method was developed for quantitatively recovering the floated metals in n-butyl acetate.

Procedures were developed for the single stage, batch ion flotation separation of several binary mixtures of the platinum metals. For these separations, conditions were adjusted in which one metal was selectively floated from the solution and recovered by a modified solvent sublation method in n-butyl acetate.

Iridium and rhodium were separated by floating the Ir(IV) from aqueous solutions of pH 2.0 with hexadecyltri-n-propylammonium bromide (HTPAB). The Rh(III) was not floated by HTPAB. Both metals were quantitatively recovered after xiii

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separation. Rhodium(III) and Ir(IV) were also separated with other surfactants from solutions of various NaCl and HCl concentrations.

Platinum and iridium were separated by reducing the iridium to Ir(III) with hydroxylamine and floating the Pt(IV) with hexadecyltri-n-butylammonium bromide (HTBAB) from solutions of 0.1 M HCl. Iridium(III) was not floated with HTBAB from 0.1 M HCl solutions. Platinum(IV) and Ir(III) were also separated with other surfactants from solutions of various NaCl and HCl concentrations.

Palladium(II) and Pt(IV) were partially separated from solutions of various initial HCl concentrations with all of the surfactant prepared for this work. Platinum(IV) was recovered free of Pd(II) from 2.0 M HCl solutions.

Palladium(II) and Pt(IV) were quantitatively separated with HTBAB from 0.01 M NH₃ solutions. The Pd(II) was converted to the cationic complex, Pd(NH₃)₄²⁺, by reaction with ammonia and was not floated by the cationic surfactants. The PtCl₆²⁻ was unaffected by the ammonia and was floated by the surfactants. Palladium(II) and Pt(IV) were also separated with other surfactants from solutions of various ammonia concentrations.
CHAPTER I
INTRODUCTION

Both laboratory and industrial scale separation procedures for the subgroup VIII elements, usually called the platinum or noble group metals, have been either tedious, time consuming, expensive or inefficient due to the similarity in properties of these elements. The cost of the metals is high; which is, in part, a result of the lack of simple, effective separation techniques. Furthermore, laboratory procedures often require the complete isolation of the individual metals from each other. Thus the search for novel separation procedures for the platinum metals remains both profitable and challenging.

Industrial procedures for separating the platinum metals are primarily concerned with their recovery from ores. A primary source of the platinum metals is the nickel-copper sulfide ore of South Africa. For processing, the ore is prepurified, cast into anodes and electrolyzed to deposit copper at the cathode, while nickel remains in solution and the platinum metals collect in the anode slimes.

The industrial recovery of the platinum metals from these anode slimes is a complicated process involving precipitation, distillation and crystallization procedures. One scheme is outlined in The Treatise on Analytical Chemistry (1) edited by I. M. Kolthoff. Initially, platinum,
gold and palladium are separated from iridium, rhodium, ruthenium, silver and osmium. Gold may be removed from palladium and platinum by reductive precipitation with iron(II) sulfate. After fusing, successively with litharge, sodium bisulfate and sodium peroxide and dissolution with various acids, the other metals are separated from each other. Ruthenium and osmium are usually recovered as the volatile tetroxides while platinum and iridium are precipitated as the ammonium salts of their hexachloro-complexes, \((NH_4)_2PtCl_6\) and \((NH_4)_2IrCl_6\), respectively.

Although improved separation techniques at any point in the group separation scheme may be beneficial, chemists have devoted most attention to the development of binary separation procedures for rhodium from iridium, iridium from platinum, and palladium from platinum (2). The emphasis on these binary separations is due to the similarity in chemical properties of the pairs, the natural occurrence of the elements in the same ores and the industrial applications of these metals in mixtures. In addition, these elements are the primary interferants in numerous analytical methods for one another. Numerous separation methods for these metals have been reviewed and described by Ginzburg (3-7) and Beamish (8,9,10).

Treatment of the noble metals with \(Cl_2\) and their subsequent dissolution in an oxidizing acid such as aqua regia results in the formation of the chlorocomplexes with
each metal in its highest stable oxidation state. Gold, platinum, palladium, iridium and rhodium are obtained as Au(III), Pt(IV), Pd(II), Ir(IV) and Rh(III), respectively. The chlorocomplex anions for these metals are $\text{AuCl}_4^-$, $\text{PtCl}_6^{2-}$, $\text{PdCl}_4^{2-}$, $\text{IrCl}_6^{2-}$ and $\text{RhCl}_6^{3-}$. It should also be noted that Pd(IV), Rh(IV) and Pt(III) are not found except under extreme conditions, but Ir(III) and Pt(II) may be easily obtained. These metals are maintained in their fully Cl-substituted forms only in strong acid. In diluted acid or neutral solutions they undergo water substitution which may result in positive or uncharged species; for example, $\text{Pd(H}_2\text{O)}_3\text{Cl}^+$, $\text{Pd(H}_2\text{O)}_4^{2+}$, etc. However, the rate of water substitution appears to be slow; for example, the half life for the first aquation of (PdCl$_4^{2-}$) is about $10^3$ seconds, but kinetic studies are incomplete. Thus, the fully chloride substituted salts may be used in weak acid if the process is fast relative to the rate of aquation.

The chlorocomplexes discussed above are easily prepared, well characterized and stable so numerous attempts have been made in utilizing them in separation schemes. It was noted earlier that the ammonium salts of PtCl$_6^{2-}$ and IrCl$_6^{2-}$ are often separated from the other noble metals by precipitation. Unfortunately, the separation is incomplete as the salts have appreciable solubility (4). Palladium and platinum may be separated from iridium and
rhodium by reduction precipitation of their complex chlorides with mercurous chloride, cuprous chloride and many other reducing agents (11). Hydroxide substitution of the chlorocomplexes of Pd(II), Rh(III) and Ir(IV) gives insoluble hydrolysis products from pH 6 to pH 8 which may be used to separate them from the soluble Pt(OH)_{6}^{2-} (12). Palladium may be separated from the other metals by precipitation with various oximes (7). Metallic copper may be used to separate rhodium from iridium (13) as it reduces the rhodium to the metal while the iridium remains in solution as IrCl_{6}^{3-}. Many other precipitation methods of lesser importance are discussed in the general references mentioned earlier.

Extraction has been utilized for separating the chlorocomplexes (2,8,14). Palladium(II), Pt(IV) and Ir(IV) form salt-like compounds with several reagents that are readily extractable. As these platinum metal chlorocomplexes are anionic, they readily react with positively charged organic radicals, such as ROH_{2}^{+}, R_{2}OH^{+}, R_{2}COH^{+}, RNH_{3}^{+}, R_{4}N^{+}, R_{4}As^{+} and R_{4}P^{+} and the resultant compounds may be extracted in various nonpolar solvents. The chlorocomplexes of Rh(III) and Ir(III) are also anionic but do not form salt-like compounds with these organic radicals and are not extracted. These properties lead to the extraction separation of Pt(IV) and Pd(II) from Ir(III) with tetraoctylammonium bromide (15), Ir(IV) from Rh(III) with tetraphenylarsonium chloride (16),
Ir(IV) from Rh(III) with diantipyrylpropylmethane (17).
Pd(II) from Rh(III) with tetraphenylarsonium iodide (18) and Pt(IV) from Rh(III) with trioctylamine hydrochloride (19).

The use of ion exchange chromatography for separating the platinum metals has been studied (20,21,22). As the chlorocomplexes are anionic, a cation exchange column may be used to quickly and efficiently remove positively charged base metals (23). Kraus (24) and Berman (22) have determined the partition coefficients for the chlorocomplexes for anion exchange resins in hydrochloric acid solution. The Pt(IV), Ir(IV), Pd(II) and Au(III) chlorocomplexes are all strongly retained on the quaternary ammonium exchanger apparently due to the formation of sparingly soluble compounds with the exchanger (5), while Rh(III) and Ir(III) exhibit little retention. The selectivity coefficient for Pd(II) significantly decreases while those of Pt(IV) and Ir(IV) vary to a lesser extent with increasing HCl concentration. Although binary mixtures of the platinum group metals can be separated on an anion exchange column, a group separation is not feasible.

Ion exchange may be used for the complete separation of RhCl$_6^{3-}$ from IrCl$_6^{2-}$ (22,25) with an anion exchange resin. It was found that the quaternary ammonium ion exchangers slightly reduce Ir(IV) to the nonretained Ir(III), thus a strong oxidizing agent such as Ce(IV) or bromine was added to keep all iridium present as Ir(IV) (26). Platinum (IV)
may be separated from iridium on an anion exchanger by reducing the iridium present to \text{Ir(III)} with hydroxylamine (27). The platinum is not reduced. Likewise, \text{Pt(IV)} has been separated from \text{Rh(III)} with an anion exchanger (28).

Even though much research has been devoted to precipitation, ion exchange, extraction and other methods of separation for the noble metals, the search for better methods continues. One separation technique, which has not been previously investigated for separating the platinum metals, is ion flotation. It was suggested as early as 1962 by Sebba (29) in his original treatise on ion flotation that the separation of this group could be accomplished by ion flotation. He established that \text{PtCl}_6^{2-} could be concentrated from dilute aqueous solution with positively charged surfactants but carried the work no further.

As ion flotation is a relatively new tool for the separations chemist (30-43), it is appropriate to present a discussion of its theory and applications. The method involves the removal of surface-inactive cations or anions from aqueous solutions by the addition of oppositely charged surfactants and the subsequent passage of gas through the solution. Bubbles rising through the solution carry the surfactant (collector) to the surface where foam forms. Due to the coulombic attraction of the ions of interest (colligend) for the collector, the ions are also carried to the surface where a solid scum, called the sublate,
forms. Flotation can occur from true solution or a surfactant-colligend salt may precipitate and be floated as a solid. In either case, the sublate is the surfactant-colligend salt which may be physically removed from the foam either mechanically or by dissolution with an organic solvent which is immiscible with the aqueous phase.

Ion flotation has its origin in the work of Langmuir and Schaefer (35). They were studying stearic acid monolayers on aqueous solution surfaces when they noted that copper(II) ions were being concentrated in these monolayers. Analysis of the monolayers indicated that copper stearate was formed. They found that the metal salt would form from solutions containing as little as $5 \times 10^{-9}$ M copper and that the concentration of copper in the monolayer increased with time. The amount of copper adsorbed was found to be dependent on the gas-liquid surface area and that effectively all the copper present in dilute solution could be removed if a large enough surface area were provided and if enough time were allowed for the Cu$^{2+}$ ions to migrate to the monolayer.

About twenty years after these initial observations, Sebba (36,37) found that the efficiency of concentrating ions from solution could be improved by providing a very large gas-liquid surface area by bubbling gas through the solution. His work included the floating of anionic uranium complexes with long hydrocarbon chain amine salts in acidic solution. Later, he extended his studies to the
flotation of many inorganic species and organic compounds and published the first book on the subject which presented brief ion flotation studies on most of the transition metals.

In order to understand the parameters influencing ion flotation, the chemistry of solutions containing surface active reagents should be understood. Therefore the behavior of surfactants and the physical properties attributed to them will now be examined.

The surface activity of the collector is the result of its structure. Surfactants consist of a long hydrocarbon chain which is hydrophobic with a terminal polar or ionic group that is hydrophilic. In the interior of a liquid, a molecule is surrounded on all sides by other molecules and thus all forces are uniform. But at the gas-liquid interface, all molecules are subjected to a strong inward force due to the difference in density of the gas phase. When a surfactant is added to an aqueous solution, molecules will migrate to the gas-liquid interface where the hydrocarbon ends will be oriented into air, while the polar ends will be directed into the solution, thus creating a thermodynamically stable situation. The surface excess of surfactant at equilibrium is given by:

\[
\Gamma = -\frac{c}{RT} \frac{\partial \gamma}{\partial c}
\]

where:

\( \Gamma \) = surface excess concentration (moles/cm\(^2\))

\( c \) = surfactant concentration in solution

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\[ R = \text{molar gas constant} \]

\[ T = \text{temperature} \]

\[ v = \text{surface tension (dynes/cm)}. \]

This equation is the Gibbs adsorption isotherm and relates the concentration of the surfactant in the gas-liquid surface to its bulk phase concentration; but it does not indicate how fast equilibrium is attained. These data may be obtained experimentally and equilibration times of 60 minutes are not unusual for ionic surfactants (30). Thus the amount of colligend floated depends on the surface excess concentration of surfactant (collector) as given by the Gibbs equation. The rate of removal will, in turn, depend on how fast the equilibrium is attained.

Another interesting property of surfactants is their ability to form micelles. When the surfactant concentration is sufficiently high, the surfactant ions can arrange themselves in another fashion which is thermodynamically stable. They do this by grouping together in a sphere so that the hydrocarbon chains are close together and directed away from the water. The hydrophilic or charged ends are in contact with the water. The group of surfactant molecules is called a micelle and may contain more than fifty units. Although micelles formed with ionic surfactants possess a charge and attract the colligend, they do not concentrate in the gas-liquid interface and therefore are detrimental to flotation.
The concentration at which micelles form is called the critical micelle concentration (CMC) and is dependent on surfactant chain length and degree of branching, ionic strength of the solution and the concentration of other organic species present (e.g. ethanol). Surfactants are usually stored in absolute ethanol to prevent the formation of micelles. For ion flotation studies the surfactant is usually added in concentrations that are below the CMC, but in many cases where the CMC is exceeded, it has been shown that the rate of micelle formation is slower than the flotation process; thus no reduction of colligend flotation is attributed to micelles (38) under these conditions.

A third property of surfactants is their ability to produce froths and foams when a gas is bubbled through a solution of the surfactant. Foams are considered to be two phase systems comprising a gas and entrained liquid. Froths contain foam, which collapses to the pure liquid phase, and some solid material. In the presence of small univalent counterions, such as Cl\(^-\), cationic surfactants usually form foam heads above the aqueous solution whereas with larger ions, such as transition metal ions, surfactants form froths which collapse to produce a sublate.

The amount of sublate and foam present in the froth is determined by the surfactant concentration, the selectivity coefficient of the surfactant for the colligend and the concentrations of all counterions present.
An excess of surfactant is desirable because some foam head is needed to support the sublate and prevent redisper­sion into the bulk solution. However, excessive surfactant concentrations and large "spectator" ion concentrations result in large, voluminous stable foam heads which reduce the effectiveness of ion flotation as a concentrating method (39,40).

The amount of surfactant carried by the bubbles into the foam with colligend or spectator counterions is governed by an ionic equilibrium. After the foam head reaches a certain height, the foam collapses and entrained liquid containing the surfactant paired with spectator ions is returned to the bulk solution, while the surfactant-colligend pairs form the sublate. This reflux action shifts the equilibrium and additional colligend is floated. Thus, the degree of removal is also governed by the stability of the foam.

For a more complete description of surface active agents and a mathematical treatment of foaming and related processes the reader is referred to J. J. Bikerman's excellent book on the subject (41). The parameters which influence the efficiency of ion flotation will now be examined.

Variables which influence the efficiency of ion flota­tion include the physical structure of the surfactant, pH, bubble size, gas flow rate, neutral salt content, initial concentration of surfactant and colligend, ethanol content,
temperature and the presence of foam breaking reagents (31,40). The most important of these are discussed below.

The length of the surfactant hydrocarbon chain is important because it governs the surface excess amount of surfactant that exists in the gas-liquid interface at equilibrium. The solubility of surfactants increases with decreasing chain length but its surface activity decreases. Longer chains increase surface activity but surfactants with excessive chain lengths are insoluble. For ion flotation, collectors with 8 to 18 units in the hydrocarbon chain are usually employed.

The pH of the solution is important because it affects the nature and charge of both the collector and colligend. The charge on the collector may change over a pH range due to hydrolysis or complex formation. Changes may occur in the ionization of the collector; acids and amines may lose their charge at low and high pH, respectively. Furthermore, the stability of the foam is greatly influenced by pH.

Nitrogen, usually used as the "carrier" gas for flotation studies, is cheap, readily purified and inert. Air and other gases generally are not used to avoid any oxidation or reduction effects that might influence the flotation process. Nitrogen supplies are usually humidified prior to passing into the flotation apparatus to reduce solvent loss due to evaporation.

Bubble size and gas flow rate influence the rate of surfactant removal from the bulk solution and the relative
amount of foam formed. Flotation studies (40) indicate that large bubble sizes result in large amounts of foam containing much entrained liquid. Small bubbles produce compact, dense foams with larger surface area, but which coalesce quickly. Fast gas flow rates also produce large amounts of foam and quickly remove surfactant from the solution. As a definite time is required for the collector-colligend pairs to form in the bulk solution due to migration of colligend to the bubble, the rapid removal of surfactant reduces the efficiency and rate of flotation. Optimum bubble sizes are produced from glass frits with a pore size of 5 to 10 microns. Optimum flow rates range from 10 mL/min to 1000 mL/min, depending on the stability of the foam.

The presence of neutral salts often decreases the efficiency of flotation due to competition between the colligend and added ions for the collector. In some cases, however, there is little or no decrease in flotation. Thus, it is possible to separate two species merely by varying ionic strength if the flotation of one is significantly depressed, while the other is unaffected.

It was mentioned earlier that the surfactants are added in ethanol. A small amount of ethanol is beneficial as it increases the efficiency and rate of flotation by slightly lowering the solution surface tension, which decreases the bubble size and increases the gas-liquid surface area. Too much ethanol decreases flotation.
efficiency (42). Usually 1 mL of absolute ethanol is added per 100 mL of solution.

When particularly stable foams are formed, a foam breaker may be used. In some cases an immiscible organic solvent is added to the top of the aqueous solution. The rising gas bubbles carry the sublate into the organic layer where it dissolves without foam formation. This process is called solvent sublation and has been reviewed by Karger (43).

Although ion flotation is an important technique for concentrating ions from dilute solutions, its real significance to the separations chemist is its selectivity. The broadest kind of selectivity is in its ability to remove ions of one sign, that is floating cations with an anionic surfactant while leaving the undesired anions in the bulk solution. It is possible to increase this selectivity by controlling the chemical nature of the solution by varying pH, ionic strength, etc. For example, a mixture of mercury(II) and iron(III) can be separated by adding enough HCl to raise the acidity to 0.3 M. The mercury can then be collected as HgCl$_3^-$, while iron remains in solution as Fe(H$_2$O)$_6^{3+}$ (44).

There is also a type of selectivity which depends upon the length of the hydrocarbon chain. Calcium will not float with sulpholausic acid (twelve carbons) but barium will. Then if the surfactant chain length is increased to
sixteen carbons, the calcium will float. It has been suggested that the separation is the result of the sublate solubility; the calcium salt of the twelve carbon chain surfactant being much more soluble that the barium salt (32).

The formation of insoluble precipitates does not always improve flotation, however. Charewicz and Walkowiak (45) were able to separate the cyano complexes of nickel(II) and cobalt(III) with cetylpyridinium chloride because the cobalt complex formed a colloidal precipitate with the surfactant which did not float, while the nickel complex was rapidly removed. The selectivity of the flotation was attributed to the magnitude of the complex ionic charge, the cyanocobaltate being a trivalent anion, while the cyanonickelate is a divalent anion.

Various attempts have been made to establish a mathematical basis for selectivity. Sebba (33) proposed that a function called the sublation constant, $F$, could be used for predicting separation. The colligend ion, $B^Y$, reacts with a stoichiometric amount of collector, $C^X$, to form a sublate salt, $SB$. Thus,

$$xA + yC = SB$$

and the sublation constant is given by

$$F = \frac{a_A^X \cdot a_C^Y}{a_{SB}} = (a_A)^X (a_C)^Y$$

where $a$ is the activity and $a_{SB} = 1$. This equation is
analogous to that obtained for the solubility product of precipitates.

It may be seen that for a two component mixture, the one with the smallest sublation constant will be floated first if starvation doses of surfactant are added. Unfortunately, the determination of sublation constants is difficult due to their very small values. In addition, the assumption that $a_g = 1$ may be invalid as the sublate does not always exist as a solid in the bulk solution. Other researchers (44,46-49) have therefore used distribution coefficients, which can be experimentally determined, for evaluating ion flotation selectivity.

Karger, et al. (44,46) have used the distribution factor, $\Gamma/C$, for evaluating the selectivity of ammonium surfactants in a recycling foam separation apparatus. $\Gamma/C$ is therefore an experimentally determined factor, where $\Gamma$ is the surface excess of solute in moles per cm$^2$ and $C$ is the bulk equilibrium concentration of solute. The values of $\Gamma/C$ are not reproducible because their derivation assumes uniform foam bubble sizes, the absence of bubble coalescence, constant gas flow rate and constant liquid reflux flow rate. Nonetheless, selectivity data obtained for several metals have been used for predicting optimum separation conditions.

Grieves and co-workers (47) have studied continuous foam fractionation for establishing selectivity coefficients analogous to those obtained for ion exchange chromatography.
For the exchange reaction in the gas-liquid interface

\[(SA)_s + B_b \rightleftharpoons (SB)_s + A_b\]

where

- \(SA\) = surfactant with "A" as counterion
- \(SB\) = surfactant with "B" as counterion
- \(A\) = an ion (e.g. \(Br^-\))
- \(B\) = colligend ion (e.g. \(AuCl_4^-\))
- \(s\) = surface layer at gas-liquid interface
- \(b\) = bulk solution

and the thermodynamic equilibrium constant for this reaction is

\[K_{\text{exchange}} = \frac{a_{SB} \cdot a_A}{a_{SA} \cdot a_B}\]

where \(a_x\) = the activities of the species present. The concentrations of \(A\) and \(B\) in the surface layer are given by

\[[A]_s = \frac{\Gamma_A}{d} \text{ and } [B]_s = \frac{\Gamma_B}{d}\]

where \(\Gamma_x\) is the surface excess of solute and \(d\) is the thickness of the interfacial layer. If the activity coefficients of \(A\) and \(B\) are assumed to be unity and all the surfactant is assumed to be in the surface layer, then the above equations can be combined to give the selectivity coefficient,

\[K' = \frac{\Gamma_B [A]_b}{\Gamma_A [B]_b}\]

where
The above selectivity coefficient could be determined by spreading a monolayer of surfactant with counterion A on an aqueous solution containing B and determining the concentration of A and B in the surface layer and bulk solution at equilibrium. It is, however, very difficult to collect a surface film without bulk solution contamination. Grieves and coworkers (47) therefore used a continuous, counter-current flotation apparatus for which the selectivity coefficient may be shown to be

\[ K' = \frac{([B]_i - [B]_r)[A]_r}{[B]_r ([A]_i - [A]_r)} \]

where i and r subscripts denote concentrations in the initial (feed) and residual (bulk) streams, respectively.

Calculations indicate a selectivity order of \( I^- > NO_3^- > Br^- \) for strongly basic ammonium surfactants. In other studies, Walkowiak and Grieves (48) established the selectivity order of common anions as being \( NO_3^- > Br^- > CN^- > Cl^- > SO_4^{2-} \) and for heavy metals as \( Au(CN)_4^- > Hg(CN)_4^{2-} > Cd(CN)_4^{2-} > Zn(CN)_4^{2-} \). Walkowiak and Rudkin (49) determined that \( Au(CN)_4^{2-} > Ag(CN)_2^- \) versus \( I^- \). It is important to note that the selectivity coefficients...
obtained in this manner must be given with reference to the initial counterion of the surfactant, e.g. $I^-$. Some researchers (45) use the enrichment ratio, $E$, as a means of indicating the efficiency of a batch flotation process. The enrichment ratio is defined as $C_f/C_r$, where $C_f$ is the concentration of the colligend in the condensed foam liquid and $C_r$ is the final concentration of the colligend in the residual solution. For example, for a solute which is 95% floated from 100 mL of a $5 \times 10^{-5}$ M solution into a condensed foam volume of 0.5 mL, the enrichment ratio is 3980. For another solute which is only 50% floated under identical conditions, the enrichment ratio falls to 199. By comparing the enrichment ratios for ions floated under identical conditions, trends in surfactant selectivity are observed. There is some difficulty in obtaining reproducible enrichment ratio values, however, as they are dependent on the foam liquid volume, which is influenced by several factors mentioned earlier.

A large number of anionic and cationic complexes have been concentrated from aqueous solutions. Some were discussed by Sebba (34) in his original book on ion flotation. Recent reviews include those of W. Charewicz and W. Walkowiak (45), Grieves (50) and Clark and Wilson (51). Karger's review (52) gave a detailed survey of principles and applications through 1968.
The separation of multicomponent mixtures has been less frequently studied. The means by which ion flotation processes are made selective for various ions are of particular interest. The separations of Hg(II) and Fe(III), Ca(II) and Ba(II), Ni(II) and Co(III) have already been discussed. By varying pH and ionic strength Rubin and Lapp (53) separated Cu(II) and Fe(II). Karger and Miller (44) also separated Co(II), Fe(III) and Hg(II) by varying the chloride concentration. Okamoto and Chou (54) selectively separated Hg(II) and Cd(II) with a chelating surfactant. Bikerman (55) has investigated the separation of Ca(II), Fe(III) and Mn(II) with alkyl sulfates. Zeithlein, et al., (56,57,58) have published several foam separation procedures for the components in seawater. Izumi (59) recovered copper, zinc, cadmium and lead selectively from industrial wastewater by varying the pH. Grieves, et al., (60,61) have studied the selective foam separations of anions. They established the selectivity sequence for metal oxyanions to be Re(VII) > Mo(VI) > Cr(VI) > W(VI) > V(V) and for common anions as SCN⁻ > I⁻ > ClO₃⁻ > Br⁻ > NO₂⁻. Walkowiak, et al., (62) have separated the chlorocomplexes of Au(III), Zn(II), Cd(II) and Hg(II) by varying the Cl⁻ concentration. Grieves and Bhattachryya (63) have studied the separation of I⁻, HCrO₄⁻, S₂O₃²⁻ and Ag(S₂O₃)³⁻. Phillips, et al., (64,65,66) have studied the foam distribution of phosphate and other anions of polyprotic acids.
Lusher and Sebba (67) separated the anionic oxalato complexes of Al(III) from Be(II) with fatty amine salts. Jacobelli-Turi, et al., (68) separated U(VI) from V(V) because uranium forms the complex, \([\text{UO}_2(\text{CO}_3)_3]^{4-}\), which can be floated. They (69) also separated U(VI) from Th(IV) in 8 M HCl with surfactants of the type \(R_4N^+\) because of the formation of anionic chlorocomplexes with uranium.

Very little research has been directed toward the separation of the platinum group metals. Charewicz and Walkowiak (45) indicated that Pt(IV) and Pd(II) could be separated with hexadecyldimethylbenzylammonium chloride but presented no data to verify their conclusion. Single metal flotation studies have been concerned with Au (50, 60, 62, 70, 71), Pd (72, 74) and Pt (73). Kepak and Kriva (75) used dodecylamine to float Ru(IV) and Ru(III). As far as could be determined, the flotation properties of iridium, osmium and rhodium have not been previously studied.

The purpose of the present work is to present an experimental investigation of the ion flotation properties of the platinum group metals and separations methods based on these properties. The anionic chlorocomplexes were chosen for study for reasons previously outlined. Ruthenium and osmium have several primary oxidation states, therefore the complex species which exist for these metals in acidic aqueous solution is complicated and not well established. Therefore, the flotation properties of ruthenium and osmium...
were not investigated as part of this work. As the ruthenium and osmium tetroxides may be removed by distillation, they do not present a major problem in the group separation.

Because the anionic chlorocomplexes were chosen for study, cationic surfactants were used for flotation. The surfactants were of the type RNR'Br, where R is the long hydrocarbon (primary) chain and R' is a shorter hydrocarbon (secondary) chain. Except in those studies where the surfactant or metal chlorocomplex is a variable, the amount of surfactant added was always greater than the calculated stoichiometric amount. In order to determine optimum conditions for the flotation and separation of the platinum group metals, studies of the influence of several variables on flotation are presented. These variables are surfactant primary chain length, surfactant secondary chain length, initial HCl concentration, initial NaCl concentration, initial surfactant concentration and initial metal chlorocomplex concentration. Other parameters discussed earlier were held constant for these studies. Batch flotation separation procedures are presented for Ir(IV) from Rh(III), Pt(IV) from Ir(III) and Pt(IV) from Pd(II). The use of solvent sublation for quantitatively recovering the metals is also discussed.
CHAPTER II
EXPERIMENTAL

A. REAGENTS

1. Noble Metal Stock Solutions.

Both radioactive and nonradioactive noble group metals were used in these procedures. The nonradioactive solutions will be described first. All metal stock solutions were prepared in aqueous HCl to avoid hydrolysis.

Standard palladium(II) solution was prepared by dissolving 2.000 grams of palladium metal filings in concentrated HCl and diluting to 1 liter with distilled and deionized water. The final solution was 2000 ppm palladium (0.0188 M as \( \text{PdCl}_4^{2-} \)) in 2 M HCl.

A platinum(IV) solution was prepared by dissolving 2.2920 grams of platinum wire in aqua regia, fuming to dryness three times with HCl and diluting to 1 liter with distilled and deionized water and hydrochloric acid. The final solution was 2292 ppm platinum (0.0117 M as \( \text{PtCl}_6^{2-} \)) in 2 M HCl.

Iridium was obtained as the sodium hexachloroiridate (IV). The salt was purified by the method of Sloth and Garner (76). The standard iridium(IV) solution was prepared containing 1474 ppm iridium (0.00767 M as \( \text{IrCl}_6^{2-} \)) in 2 M HCl. Iridium(III) solutions were prepared as needed from the iridium(IV) solutions by heating an aliquot of the iridium(IV) with an aliquot of 10% hydroxylamine hydro-
chloride on a steam bath for 10 minutes.

Standard rhodium(III) solution was prepared by dis­solving sodium hexachlororhodate in 6 M HCl and refluxing for six hours to ensure complete conversion to RhCl$_6^{3-}$. The solution was prepared as 817 ppm Rhodium (0.00797 M as RhCl$_6^{3-}$) in 6 M HCl.

A standard gold(III) solution was prepared by dis­solving 1.816 grams of gold wire in aqua regia, fuming with concentrated HCl to dryness three times and diluting to 1 liter with deionized and distilled water and hydro­chloric acid. The final solution was 1816 ppm gold (0.00922 M as AuCl$_4^{-}$) in 2 M HCl.

Thermal neutron activation of the platinum metals was used to produce radiotracers for these metals by (n,$\gamma$) reactions. Californium-252 was used as a neutron source. Radioactive tracers for Pt(IV), Pd(II) and Au(III) were produced by activating aliquots of the above stock solutions. Radioactive iridium was prepared by the neutron activation of solid sodium hexachloroiridate(IV) and a second stock solution was prepared from the radioactive salt in the same manner as was the stable stock solution. Radioactive Ir(III) was prepared by reducing the radioactive Ir(IV). Aliquots of these solutions containing either radioactive Pt(IV), Pd(II), Au(III), Ir(III) or Ir(IV) were used in the flota­tion experiments when tracers needed to be employed.

All the tracers used in these studies are summarized in Table I. The specific activities are also listed as
<table>
<thead>
<tr>
<th>Radioisotope</th>
<th>Half Life</th>
<th>Activation Time</th>
<th>Major Energies (MeV)</th>
<th>Activity (CPM) for 5 mL of 5 x 10^-5 M</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rh-104m</td>
<td>4.35m</td>
<td>1 hour</td>
<td>0.078, 0.057</td>
<td>- - -</td>
</tr>
<tr>
<td>Pd-109</td>
<td>13.43h</td>
<td>1 week</td>
<td>0.088</td>
<td>~1000</td>
</tr>
<tr>
<td>Ir-192</td>
<td>74.2d</td>
<td>1 month</td>
<td>0.316, 0.468</td>
<td>~30,000</td>
</tr>
<tr>
<td>Ir-194</td>
<td>19.2h</td>
<td></td>
<td>0.328</td>
<td></td>
</tr>
<tr>
<td>Pt-195m</td>
<td>4.0d</td>
<td>1 week</td>
<td>0.031, 0.099</td>
<td>~800</td>
</tr>
<tr>
<td>Pt-197</td>
<td>18.3h</td>
<td>1 week</td>
<td>0.077, 0.191</td>
<td></td>
</tr>
<tr>
<td>Au-198</td>
<td>64.8h</td>
<td>2 weeks</td>
<td>0.412</td>
<td>~10,000</td>
</tr>
</tbody>
</table>
well as the total counts obtained from 5 mL of $5 \times 10^{-5}$ M solution with a well-type NaI(Tl) detector of 30% efficiency. The activities for Pt(IV), Pd(II) and Au(III) represent the counts obtained after activation to saturation and a 6 hour decay to eliminate activity due to $^{38}$Cl (37 minute half life).

The activity for iridium represents the counts obtained after a 4 week activation time and 6 day decay time to eliminate activity due to $^{24}$Na (15 hour half life).

It may be seen that the only radioisotope produced for rhodium has a half life that is too short to be useful for these studies. In addition, due to relatively short half lives of the radioisotopes for platinum and palladium, aliquots of these metals had to be activated frequently in order to keep a supply on hand for these studies.


Positively charged surfactants were used to float the anionic chlorocomplexes of the platinum metals. These surfactants, which are quaternary ammonium salts, were prepared by refluxing the long chain alkyl bromides with excess tertiary amines in absolute methanol for 18 hours.

$$RBr + NR_3^+ \xrightarrow{\Delta} RNR_3^-$$

For surfactants of the type $RNR_3^+ Br^-$, $R$ is called the surfactant primary chain and $R'$ is called the surfactant secondary chain. The methanol was removed by rotary evaporation at 70°C for 2 hours and the salts were re-
crystallized twice from absolute ethanol - ethyl ether at 0°C. After vacuum drying at 78°C over P₂O₅ for 24 hours the surfactants were prepared as 0.10 M solutions in absolute ethanol. The long chain alkyl bromides were purchased from Eastman and were found to be > 98% pure by gas chromatography on a 5% OV-1, 100/110 mesh anarkrom Q, 0.5 in. x 6 ft. column operated at 170°C. The amines and pyridine were purchased from Aldrich and were used immediately without further purification.

In addition, hexadecylamine was obtained from Eastman and reacted with anhydrous HCl in absolute ether to give the amine salt. The hexadecylammonium chloride (HAC) was purified by the same procedure and prepared as a 0.05 M solution in absolute ethanol.

For primary chain length studies the fatty alkyl bromides of hydrocarbon chain length C-8, C-10, C-12, C-14, C-15, C-16 and C-18 were refluxed with trimethylamine to produce octyltrimethylammonium bromide (OTMAB), decyltrimethylammonium bromide (DTMAB), tetradecyltrimethylammonium bromide (TTMAB), pentadecyltrimethylammonium bromide (PTMAB), hexadecyltrimethylammonium bromide (HTMAB) and octadecyltrimethylammonium bromide (ODTMAB), respectively.

Surfactants of the type RNH₃⁺, RN(Me)₃⁺, RN(Et)₃⁺, RN(Pr)₃⁺ and RN(Bu)₃⁺ were prepared for studies of the influence of the chain length of secondary ammonium substituents on flotation. HAC and HTMAB were mentioned...
above. Triethylamine, tripropylamine and tributylamine were refluxed with hexadecylbromide to give hexadecyltriethylammonium bromide (HTEAB), hexadecyltripropylammonium bromide (HTPAB) and hexadecyltributylammonium bromide (HTBAB), respectively.

All surfactants prepared for this work are summarized in Table II.

3. Other Reagents.

A 3.0 M NaCl stock solution was prepared by dissolving 350.6 grams of salt in 2 liters of distilled water.

A 6 M HCl solution was prepared by diluting 500 mL of concentrated HCl (12 M) to 1 L with distilled water.

1 M tin(II) chloride solution was prepared by dissolving 112.8 grams of reagent grade stannous chloride (SnCl₂·2H₂O) in 200 mL of the 6 M HCl solution, filtering and bringing up to 0.5 liter with enough additional HCl added to make the solution 3.5 M HCl. The solution was deoxygenated with nitrogen gas and prepared fresh weekly.

A 1% cerium(IV) bisulfate solution was prepared by dissolving 10 grams of cerium(IV) bisulfate in a mixture of 100 mL of sulfuric acid and 500 mL of distilled water, cooling and diluting to 1 L.

A 1% dimethylglyoxime (DMG) solution was prepared by dissolving 10 grams of DMG in 1 L of 95% ethyl alcohol.

A 1 M NH₃·H₂O solution was prepared by diluting 69 mL of concentrated ammonium hydroxide (14.5 M) to 1 L with distilled water.

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<table>
<thead>
<tr>
<th>Surfactant</th>
<th>Abbreviation</th>
<th>Theoretical</th>
<th>Found</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>%C  %H  %N</td>
<td>%C  %H  %N</td>
</tr>
<tr>
<td>hexadecylamine hydrochloride</td>
<td>HAC</td>
<td>69.41 12.78 5.06</td>
<td>69.72 12.58 4.92</td>
</tr>
<tr>
<td>hexadecyl trimethyl ammonium bromide</td>
<td>HTMAB</td>
<td>62.62 11.62 3.84</td>
<td>62.77 11.13 3.76</td>
</tr>
<tr>
<td>hexadecyl triethyl ammonium bromide</td>
<td>HTEAB</td>
<td>65.00 11.90 3.44</td>
<td>64.96 11.85 3.22</td>
</tr>
<tr>
<td>hexadecyl tripropyl ammonium bromide</td>
<td>HTPAB</td>
<td>66.93 12.13 3.12</td>
<td>67.06 11.65 3.05</td>
</tr>
<tr>
<td>hexadecyl tributyl ammonium bromide</td>
<td>HTBAB</td>
<td>68.54 10.27 2.85</td>
<td>68.19 10.01 2.55</td>
</tr>
<tr>
<td>octyl trimethyl ammonium bromide</td>
<td>OTMAB</td>
<td>52.38 10.38 5.55</td>
<td>52.51 10.02 5.13</td>
</tr>
<tr>
<td>decyl trimethyl ammonium bromide</td>
<td>DTMAB</td>
<td>55.71 10.79 5.00</td>
<td>55.86 10.61 4.89</td>
</tr>
<tr>
<td>dodecyl trimethyl ammonium bromide</td>
<td>DDTMAB</td>
<td>58.43 11.11 4.54</td>
<td>58.32 10.86 4.48</td>
</tr>
<tr>
<td>tetradecyl trimethyl ammonium bromide</td>
<td>TTMAB</td>
<td>60.70 11.39 4.16</td>
<td>61.01 11.40 4.06</td>
</tr>
<tr>
<td>pentadecyl trimethyl ammonium bromide</td>
<td>PTMAB</td>
<td>61.70 11.50 4.00</td>
<td>62.24 11.42 3.90</td>
</tr>
<tr>
<td>octadecyl trimethyl ammonium bromide</td>
<td>ODTMAB</td>
<td>64.26 11.81 3.57</td>
<td>64.13 11.38 3.46</td>
</tr>
</tbody>
</table>
A 10% hydroxylamine hydrochloride (NH₂OH·HCl) solution was prepared by dissolving 100 grams of the salt and diluting to 1 L with distilled water.

B. APPARATUS

1. Flotation System

There are no commercially produced flotation systems, thus each researcher must build his own. The flotation system can be quite simple requiring only a gas supply such as air or nitrogen and a container (flotation cell or column) in which to place the sample solutions, where bubbles are generated from the gas supply. A typical flotation cell can be an ordinary glass Buchner funnel with a fritted glass disc to provide small gas bubbles. However, a more complicated system was used for these studies in order to avoid problems due to a lack of pressure and flow control.

The general flotation system is illustrated in Figure I. The gas supply was from a pressure regulated nitrogen tank. The nitrogen gas was filtered to remove impurities and humidified by passing through water to avoid any possible sample solution evaporation. The nitrogen flow was regulated with a rotameter at a flow rate of 10 cc min⁻¹ which was found to be the optimum for these studies. Foam overflow from the flotation cell was removed with an aspirator and condensed in a receiving vessel containing 2-octanol.
FIGURE I

THE FLOTATION SYSTEM
MERCURY U - TUBE MANOMETER

LOW-FLOW-RATE CONTROLLER

FLotation Cell

FINE SINTERED GLASS FRIT

HUMIDIFIER FILTER

ROTAMETER

N₂
2. Flotation Cell or Column

There are two primary considerations for the design of a flotation cell: the glass frit pore size and the cell height. The pore size of the frit in the cell governs the size of the bubbles produced. Frits with small pores produce small bubbles with large unit volume surface area and compact foams while frits with large pores produce large bubbles with smaller unit volume surface area and larger volumes of foam. The height of the cell is important because of foam stability. Stable foams produced in short cells will be lost to overflow and therefore unavailable for reflux action. The cells made for these studies were either 15 cm or 30 cm in height and contained a fine (4-5.5 micron) frit to produce small bubbles.

A flotation cell made for these studies is illustrated in Figure II. The cell A was made by lengthening an ordinary fritted glass buchner funnel. A sample outlet B with a stopcock D was added to drain the cell. Nitrogen was passed through the sample solution in the cell by opening stopcock C. A capillary tube E was built into the cell for the addition of sample solution from reservoir F. A septum (not shown) was built into the side of the cell so that samples could be removed with a syringe. The top of the cell was constricted to avoid spillage of any foam overflow.
FIGURE II

THE FLOTATION CELL
3. **Other Apparatus**

The activities of aliquots of solutions containing radiotracers were determined with a 2 x 2" NaI(Tl) well crystal scintillation detector. The associated electronics included a high voltage power supply and a TMC 401D Multichannel Analyzer. The well in the detector was designed to hold a 2 dram (7 mL) plastic vial for counting. The detector was approximately 30% efficient and a background count rate of 400-500 CPM was observed. Total counting times were usually one to ten minutes and the results were displayed as a digital readout on an Ortec 775 counter coupled to the multichannel analyzer.

Spectrophotometric measurements were made with matched quartz cuvettes and a Beckman DB spectrophotometer or a Cary 14 recording spectrophotometer.

C. **EXPERIMENTAL PROCEDURES**

1. **Preparation of Sample Solutions for Flotation**

In order to determine the optimum conditions for flotation and separation, each noble metal was studied with respect to the variables discussed in Chapter I. Parameters that were not varied were nitrogen flow rate, bubble size, ethanol content and temperature. A discussion of the flotation data obtained for all the metals studied is presented in Chapter III.

Sample solutions were prepared from the stock solutions discussed above. The concentration of all solutes present
in each sample for flotation was dependent on which variable was under investigation; all others being held constant. In the general case, all sample solutions [except those containing Ir(IV)] were prepared in a 100 mL volumetric flask by adding enough of one of the metal chlorocomplex solutions to give a final concentration of $5 \times 10^{-5}$ M. An additional aliquot of HCl was added to give a final concentration of 0.01 M HCl. Exactly 1 mL of a 0.02 M ethanolic surfactant stock solution was then added by pipet and the solution brought to volume and mixed for 10 minutes prior to flotation. The total ethanol added in all experiments was 1 mL per 100 mL solution.

For the Ir(IV) studies, an additional step was involved in the preparation of samples. Quaternary ammonium functional groups have been shown to partially reduce Ir(IV) to Ir(III) (26). In order to counteract the reducing effect of the surfactants, 0.25 mL aliquots of a 1% cerium (IV) bisulfate solution in 10% sulfuric acid was added to both the surfactant and the Ir(IV) before mixing. In addition the Ir(IV):Ce(IV) mixture was heated for several minutes in a 140° oil bath before mixing with the surfactant.

For studies involving the length of the primary and secondary chains of the quaternary ammonium surfactants on the flotation of the platinum group metals, the sample solutions were prepared as in the general case with various surfactants.
For studies involving the influence of HCl or NaCl concentration on flotation, the sample solutions were also prepared as in the general case with selected surfactants. In addition, aliquots of stock solutions of HCl or NaCl were added to give final concentrations ranging from 0.01 to 3.0 M in 100 mL.

For studies involving the variation of surfactant concentration, sample solutions were prepared as in the general case except that aliquots of a selected surfactant stock solution for each metal were added to give concentrations ranging from 0 to 0.001 M in 100 mL.

For studies involving the variation of metal chlorocomplex concentration, sample solutions were prepared by adding exactly 1 mL of 0.1 M selected surfactant stock solution and aliquots of metal chlorocomplex solutions to give final metal concentrations ranging from 0 to 0.0015 M in 100 mL.

After the flotation properties of the platinum metals were studied, mixtures of several of these metals were prepared for flotation separation using the same procedures described above. The results for the flotation separations of Rh(III) and Ir(IV), Ir(III) and Pt(IV) as well as Pd(II) and Pt(IV) are presented in Chapter IV.

2. Estimation of the Extent of Flotation

The progress of a flotation experiment may be followed by monitoring the concentration of solute remaining in the
bulk solution with time. One to five mL samples were removed by a syringe or pipet from the flotation cell and analyzed by the methods discussed below to determine the concentration \((C_t)\) remaining in the bulk solution at any time, \(t\). By dividing \(C_t\) by the original concentration \((C_0)\) and by plotting the ratio \(C_t/C_0\) versus the flotation time, rate of removal curves are obtained. The percentage of metal floated is given by

\[
\% \text{ Floated} = [1 - (C_t/C_0)] \times 100.
\]

3. **Analytical Methods Used for Estimating the Extent of Flotation**

a. **Tracers**

The use of radiotracers provides a rapid, simple means for analyzing platinum metal solutions; however, the cost of these tracers is high. Therefore the isotopes were prepared by neutron activation as described above. The tracers produced for Ir and Au were the most useful. The half-lives of the tracers of Pt and Pd were relatively short, so new tracers had to be frequently prepared. All tracers are listed in Table I.

Metal ion concentrations in the flotation cell were determined by withdrawing aliquots from the cell and counting for 1 minute intervals. Samples of low activity were counted for longer periods for better precision. The specific activity of the aliquots is given by counts per unit time per unit volume. As the activity of the solution
is proportional to the concentration of radioactive material present, the number of counts per unit time is proportional to concentration; therefore,

\[
\frac{C_t}{C_o} = \frac{S.A._t}{S.A._o} = \frac{(\text{counts})_t}{(\text{counts})_o}
\]

where

- \(C_o\) = original concentration of solute
- \(C_t\) = concentration of solute at any time, \(t\)
- S.A. = specific activity

b. Spectrophotometric Methods

Spectrophotometric procedures were also used for estimating the extent of flotation because neutron activation does not yield a long lived isotope for Rh and tracers were not always available for Pt, Pd, Ir and Au. When spectrophotometric methods were used, calibration plots of absorbance verses concentration of standard solutions were used to determine \(C_t\).

Only the methods used on a routine basis are presented. Other methods worthy of mention include: o-dianisidine (77) and leucocrystal violet (78) for Ir(IV); thiourea (spectrophotometric) (79), thiourea (polarographic) (80) and ammonia (polarographic) (81) for Pd(II); nitrosodimethylaniline (82) for Pt(IV) and thiourea (polarographic) (80) for Rh(III).

Stannous chloride reacts with most of the platinum group metals to produce colored products. Spectrophotometric procedures utilizing stannous chloride have been
extensively studied for palladium, platinum and rhodium. These procedures were modified for use in monitoring the ion flotation process.

The original paper (83) on the determination of palladium with Sn(II) indicated a working range of 8 to 32 ppm. As the flotation procedures involved concentrations of PdCl$_4^{2-}$ of 5 ppm and less, the method was improved to yield lower detection limits. For the analysis of palladium, 5 mL of solution were removed from the flotation cell and transferred to a 10 mL volumetric flask. A predetermined amount of concentrated HCl and 1 mL of 1 M tin(II) chloride in 3.5 M HCl was then added and the flask placed in a boiling water bath for 10 minutes. The solution was cooled and diluted with a final acidity of 3-4 M HCl. The absorbance was measured versus a reagent blank at 340 nm. The complex is extractable into ethyl acetate in which its wavelength maximum shifts to 355 nm. The method cannot be used when other platinum metals are present.

Sandell's stannous chloride method for platinum (84) was also adapted for monitoring flotation. The procedure was the same as for palladium except that it is unnecessary to heat the solution. The absorbance was measured versus a reagent blank at 400 nm and the complex is extractable. Other platinum metals interfere.

Rhodium was also determined using a stannous chloride method (85,87). The procedure was the same as that used.
for palladium and the absorbance was measured at 470 nm. The procedure is useful for mixtures of rhodium and iridium because the iridium is reduced to the colorless Ir(III) by tin(II) chloride. The method may be made more sensitive by adding potassium iodide by the method of Berg and Youmans (88), but then suffers from interference due to iridium.

Although all the platinum metal chlorocomplexes are colored, only the color of the hexachloroiridate(IV) is sufficiently intense for use in the spectrophotometric analysis of dilute solutions (89). The method is useful for mixtures because the complex chlorides of Rh(III), Pt(IV), Pd(II) and Au(III) do not absorb in this region. The absorbance of the reddish brown iridium solution is measured at 492 nm. The Ir(IV) solution is prepared in HCl and mixed with an oxidizing agent.

Gold may also be determined with stannous chloride (86). The solution is prepared as above except that the final concentration of HCl is 1 M and heating is unnecessary; the color develops after twenty minutes.

c. Analysis of Platinum Metal Mixtures

There are very few analytical methods useful for the simultaneous determination of mixtures of the noble metals because of their similar chemical properties. Even the gamma-spectrometry of the radioisotopes of the platinum metals requires high resolution detectors because the peak energies are nearly identical (Table I). Therefore,
mixtures of the platinum metals often require tedious separation procedures before analysis.

The separation procedures presented in Chapter IV are concerned mainly with iridium from rhodium, platinum from iridium and platinum from palladium. Therefore, procedures for the determination of these binary mixtures will now be given.

The mixture of rhodium and iridium was determined for rhodium by the stannous chloride method described above. The iridium was determined as the radioactive tracer and did not interfere in the determination of rhodium.

The mixture of iridium and platinum was determined for platinum by the stannous chloride method. The amount of iridium was determined as the tracer; and, as Ir(III) had a significant absorption at the working wavelength of 400 nm, a suitable reagent blank was prepared for determining the absorbance due to platinum.

The mixture of platinum and palladium required a separation before analysis. A known volume of the mixture was removed from the flotation cell and made up in a volumetric flask in 2 M HCl. One mL of 1% dimethylglyoxime in 95% ethanol was added to an aliquot of this solution in a separatory funnel, and the palladium-DMG complex precipitated within 30 minutes. The Pd(DMG)$_2$ complex was extracted twice with 5 mL portions of chloroform and diluted to a known volume. The absorbance of the palladium complex was measured.
versus a reagent blank at 295 nm and the concentration of palladium determined from a calibration curve. The aqueous layer was then analyzed for platinum by the stannous chloride method discussed above.

4. **Recovery of Floated Metals**

a. **Recovery from Foam**

The quantitative recovery of sublate from the foam in a flotation process presents a problem because of the physical nature of the foam and the possibility of contamination by the bulk liquid. The foam or froth is a gas-solid-liquid dispersion which contains the sublate and original liquid. If the process involves a separation of floated and unfloated material, then the degree of contamination increases as the volume of interstitial liquid increases.

Samples of 200 mL were prepared for recovery studies. Exactly 100 mL of each solution was pipetted into the cell for flotation. Upon completion of the procedure, the sublate was recovered by several methods. One way of recovering the sublate was by removal with a spatula. Usually contamination was low, but recoveries were poor.

Results were improved by first draining the bulk liquid below the foam head. Then the foam was rinsed from the cell with acetone and collected. Contamination was greater but nearly 100% of the colligend was recovered.
b. **Solvent Sublation**

A simpler method for collecting sublate without contamination by the residual liquid involved the addition of an immiscible organic solvent in which the sublate is soluble. When a solvent is added at the beginning of the flotation process and the sublate is carried directly into it without foam formation, the process is termed solvent sublation. Solvent sublation studies require very slow gas flow rates (43), otherwise the surfactant is quickly carried into the organic layer where it dissolves and cannot return to the aqueous layer for collection, thus reducing the degree of flotation.

The percentage of metal floated was found to be reduced when solvent sublation was used, because the surfactant paired with the spectator ions (e.g. Cl⁻) was also carried into the organic layer and dissolved and thus could not return to the aqueous layer by reflux action for additional flotation. For complete recovery of colligend an adaptation of the solvent sublation process was used. The materials were mixed and floated as described above until the steady state was attained. Then an organic solvent, n-butyl acetate, was added to condense the foam and dissolve the sublate. Bubbling was again commenced to float any sublate that had been returned to the residual liquid when the organic layer was added. The two layers were then easily separated and analyzed.
c. Recovery Analytical Procedures

After separating the foam or organic layer from the residual aqueous liquid, each was analyzed in order to determine the amount of colligend floated and recovered. For determining Rh and Ir the spectrophotometric and tracer methods described before were used. Tritimetric methods were used for Pt(90), Au(91) and Pd(92) for improved accuracy.

The aqueous (bulk) solution was transferred to a beaker and boiled to dryness with 10 mL of concentrated HCl. The residual salts were then redissolved and made up in a known volume of 2 M HCl for analysis.

The organic solvent was evaporated from the floated material with a rotary evaporator. The residue was wet ashed with nitric acid and residual carbon was oxidized to CO₂ by the addition of small amounts of 30% H₂O₂. The solution was then evaporated to dryness with 10 mL of concentrated HCl and the residual salts were redissolved and made up in a known volume of 2 M HCl for analysis.

The results for metals recovered by ion flotation from dilute solution are discussed in Chapter III. The results for mixtures of metals separated by ion flotation and recovered by these procedures are discussed in Chapter IV.
CHAPTER III

ION FLOTATION STUDIES FOR THE CHLOROCOMPLEXES OF Pd(II), Ir(IV), Pt(IV), Au(III), Rh(III) AND Ir(III)

The ion flotation properties of each of the platinum group metals were surveyed with respect to several variables in order to determine the optimum flotation conditions for concentrating, recovering and separating these metals from dilute solution.

A. INFLUENCE OF PRIMARY CHAIN LENGTH

The degree of flotation of colligend is dependent on the surface excess concentration of collector in the gas-liquid interface. Since the surface excess concentration is dependent on the hydrocarbon chain length of the collector, the degree of flotation of colligend should vary in a series of flotation studies with collectors of different hydrocarbon chain lengths. In a previous study (93), variations in the chain length of surfactants were shown to significantly influence the flotation of particulates. As far as could be determined, no studies have surveyed the influence of surfactant primary chain length on ion flotation. Therefore, the ion flotation studies of the platinum group metals were begun by floating each anionic metal chlorocomplex with cationic surfactants of the type, RN(CH₃)₃Br, where R was an unbranched saturated hydrocarbon chain of 8, 10, 12, 14, 15, 16 or 18 carbons.

Figures III to VIII present the rate of removal curves.

47
FIGURE III

FLOTATION OF Pd(II): INFLUENCE OF SURFACTANT PRIMARY CHAIN LENGTH

Initial Flotation Conditions: \([\text{Pd(II)}] = 5 \times 10^{-5} \text{M},\)
\([\text{Surfactant}] = 2 \times 10^{-4} \text{M},\) pH = 2.0, 100 mL sample solutions, N\(_2\) flow rate = 10 cc min\(^{-1}\).
Surfactant Chain Length Studies

\[ \text{PdCl}_4^{2-} \]
FIGURE IV

FLOTATION OF Ir(IV): INFLUENCE OF SURFACTANT PRIMARY CHAIN LENGTH

Initial Flotation Conditions: [Ir(IV)] = 5x10^{-5} M,
[Surfactant] = 2x10^{-4} M, pH = 2.0, 100 mL sample solutions, N_2 flow rate = 10 cc min^{-1}.
IrCl$_6^{2-}$: Surfactant Chain Length Studies
FIGURE V
FLOTATION OF Pt(IV): INFLUENCE OF SURFACTANT PRIMARY CHAIN LENGTH

Initial Flotation Conditions: [Pt(IV)] = 5x10^{-5} M, [Surfactant] = 2x10^{-6} M, pH = 2.0, 100 mL sample solutions, N_2 flow rate = 10 cc min^{-1}.
FIGURE VI

FLOTATION OF Au(III): INFLUENCE OF SURFACTANT PRIMARY CHAIN LENGTH

Initial Flotation Conditions: $[\text{Au(III)}] = 5 \times 10^{-5} \text{M}$,

$[\text{Surfactant}] = 2 \times 10^{-4} \text{M}, \text{pH} = 2.0$, 100 mL sample solutions, $N_2$ flow rate = 10 cc min$^{-1}$. 

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FIGURE VII

FLOTATION OF Rh(III): INFLUENCE OF SURFACTANT PRIMARY CHAIN LENGTH

Initial Flotation Conditions: \([\text{Rh(III)}] = 5 \times 10^{-5} \text{M}, \]
\([\text{Surfactant}] = 2 \times 10^{-4} \text{M}, \text{pH} = 2.0, 100 \text{ mL sample solutions, } \text{N}_2 \text{ flow rate} = 10 \text{ cc min}^{-1}. \)
FIGURE VIII

FLOTATION OF Ir(III): INFLUENCE OF
SURFACTANT PRIMARY CHAIN LENGTH

Initial Flotation Conditions: \([\text{Ir}(\text{III})] = 5\times 10^{-5}\, \text{M},\]
[Surfactant] = 2\times 10^{-4}\, \text{M}, \text{pH} = 2.0, 100 \, \text{mL sample solutions, } N_2 \text{ flow rate} = 10 \, \text{cc min}^{-1}.

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IrCl₆³⁻: Surfactant Chain Length Studies
obtained when the anionic chlorocomplexes of Pd(II), Ir(IV), Pt(IV), Au(III), Rh(III) and Ir(III) are floated with each of the above surfactants. Because it was important to evaluate ion flotation as a method for concentrating the platinum metals from dilute solution, initial metal concentrations were $5 \times 10^{-5}$ M, which is less than 10 ppm for all of the metals. The initial surfactant concentration was $2 \times 10^{-4}$ M, which provides an excess of the stoichiometric amount for each metal.

Precipitates were observed to form prior to flotation when Pd(II), Ir(IV), Pt(IV) and Au(III) were mixed with surfactants of 12 carbon chain length or greater. Rh(III) and Ir(III) formed precipitates only with the 16 and 18 carbon chain surfactants. None of the precipitated metals could be recovered quantitatively by filtration.

The flotation curves shown in Figures III to VIII indicate that a steady state is usually attained in 30 minutes. As the chain length increases the time required for reaching steady state also increases. In addition, the fraction of metal chlorocomplex floated generally increases with increasing chain length, reaches a maximum and then begins to decrease. In order to explain these trends, several properties of surfactants will be discussed.

As the length of the primary chain of a surfactant increases, the surface excess concentration also increases. Thus it follows that the amount of colligend floated also
increases with chain length. However, the stability of the foam head formed by bubbling gas through the solution is proportional to chain length. Foam heads are desirable because they support the sublate and prevent redispersion into the bulk solution; however, very stable heads result in lower fractions of metal floated because much of the surfactant is entrained in the foam and is unavailable for collecting the colligend by reflux action.

The low flotation observed for the C-8 and C-10 surfactants may be attributed to their low surface activity and to the formation of unstable foam heads. The optimum chain lengths for maximum flotation appear to be C-14 or C-15. For C-16 and C-18 surfactants the degree of flotation generally decreases because of the formation of stable foams. As the foam stabilities increase, longer times for reaching steady state are observed because the rate of surfactant reflux is slower.

Finally, the selectivity sequence for each surfactant may be evaluated by noting the maximum percentage of each metal chlorocomplex floated as shown in Table III. The percentage floated for each of the metals studied except Au(III) reaches a maximum within two hours. Within four hours, the percentage of Au(III) floated by the C-15 surfactant was 100%, and 95% for the C-12, C-14 and C-16 surfactants, respectively. Generally, the selectivity sequence at steady state is Au(III) > Pd(II), Pt(IV), Ir(IV) > Ir(III) > Rh(III).
### TABLE III

MAXIMUM PERCENTAGE OF EACH OF THE PLATINUM METALS FLOATED WITH SURFACTANTS OF VARYING PRIMARY CHAIN LENGTH

**Initial Flotation Conditions:** [Metal] = 5x10^{-5} M, [RN(CH_{3})_{3}Br] = 2x10^{-4} M. Flotation time = 2 hours for Pd(II), Ir(IV), Pt(IV), Rh(III) and Ir(III). Flotation time = 4 hours for Au(III). Solution pH = 2.0.

<table>
<thead>
<tr>
<th>R</th>
<th>Surfactant</th>
<th>Pd(II)</th>
<th>Ir(IV)</th>
<th>Pt(IV)</th>
<th>Au(III)</th>
<th>Rh(III)</th>
<th>Ir(III)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C8</td>
<td>OTMAB</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>53</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>C10</td>
<td>DTMAB</td>
<td>10</td>
<td>11</td>
<td>10</td>
<td>65</td>
<td>0</td>
<td>10</td>
</tr>
<tr>
<td>C12</td>
<td>DDTMAB</td>
<td>41</td>
<td>98</td>
<td>93</td>
<td>95</td>
<td>10</td>
<td>30</td>
</tr>
<tr>
<td>C14</td>
<td>TTMAB</td>
<td>72</td>
<td>97</td>
<td>94</td>
<td>95</td>
<td>20</td>
<td>50</td>
</tr>
<tr>
<td>C15</td>
<td>PTMAB</td>
<td>10</td>
<td>90</td>
<td>96</td>
<td>100</td>
<td>22</td>
<td>50</td>
</tr>
<tr>
<td>C16</td>
<td>HTMAB</td>
<td>98</td>
<td>84</td>
<td>82</td>
<td>95</td>
<td>25</td>
<td>55</td>
</tr>
<tr>
<td>C18</td>
<td>ODTMAB</td>
<td>92</td>
<td>75</td>
<td>50</td>
<td>88</td>
<td>30</td>
<td>50</td>
</tr>
</tbody>
</table>
Although it was not obvious how these surfactants could be used for separating the platinum group metals, the data indicate that the quaternary ammonium surfactants are useful for concentrating the metals from dilute solutions. It was necessary to continue the studies of the flotation properties of the platinum metals with other variables before recovery and separation methods could be suggested.

B. INFLUENCE OF SECONDARY CHAIN LENGTH

Because of the significant variations in the rate and efficiency of flotation for the platinum metals with varying surfactant primary chain length, it was decided to study the effects of flotation of various secondary chain lengths. The results obtained by floating each metal with surfactants of the type $\text{C}_{16}\text{H}_{33}\text{NR'}_3^+$, where $\text{R'}$ was either $-\text{H}$, methyl, ethyl, propyl or butyl groups are discussed in this section. The hexadecyl group was chosen for the primary chain because significant flotation was observed for all the platinum metals with $\text{C}_{16}\text{H}_{33}\text{N(CH}_3)_3\text{Br}$ in the initial studies.

Figures IX to XIV present the rate of removal curves for each of the platinum group metals floated with the above surfactants. The maximum percentage of each metal floated after two hours was determined and is plotted versus secondary chain length in Figure XV. The rate of removal curves indicate that all of the metals except Au(III) are floated to the maximum value within 60 minutes. The flotation of Au(III) reaches steady state within four
FIGURE IX
FLOTATION OF Pd(II): INFLUENCE OF SURFACTANT SECONDARY CHAIN LENGTH

Initial Flotation Conditions: \([\text{Pd(II)}] = 5 \times 10^{-5} \text{M},\) \([\text{Surfactant}] = 2 \times 10^{-4} \text{M}, \text{pH} = 2.0, 100 \text{ mL sample solutions, } \text{N}_2 \text{ flow rate} = 10 \text{ cc min}^{-1} \).
FIGURE X

FLOTATION OF Ir(IV): INFLUENCE OF SURFACTANT SECONDARY CHAIN LENGTH

Initial Flotation Conditions: \([\text{Ir(IV)}] = 5\times10^{-5} \text{M},\]
\([\text{Surfactant}] = 2\times10^{-4} \text{M}, \text{pH} = 2.0, 100 \text{ mL sample solutions, } \text{N}_2 \text{ flow rate} = 10 \text{ cc min}^{-1}.\)
FIGURE XI

FLOTATION OF Pt(IV): INFLUENCE OF SURFACTANT SECONDARY CHAIN LENGTH

Initial Flotation Conditions: \([\text{Pt(IV)}] = 5 \times 10^{-5} \text{M},\)
\([\text{Surfactant}] = 2 \times 10^{-4} \text{M}, \text{pH} = 2.0, 100 \text{ mL sample solutions, } N_2 \text{ flow rate} = 10 \text{ cc min}^{-1} \).
FIGURE XII

FLOTATION OF Au(III): INFLUENCE OF
SURFACANT SECONDARY CHAIN LENGTH

Initial Flotation Conditions: \([\text{Au(III)}] = 5 \times 10^{-5} \text{M,}\)
\([\text{Surfactant}] = 2 \times 10^{-4} \text{M,}\) pH = 2.0, 100 mL sample
solutions, \(\text{N}_2\) flow rate = 10 cc min\(^{-1}\).

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FIGURE XIII
FLOTATION OF Rh(III): INFLUENCE OF SURFACTANT SECONDARY CHAIN LENGTH

Initial Flotation Conditions: \([\text{Rh(III)}] = 5 \times 10^{-5} \text{M},\]
\([\text{Surfactant}] = 2 \times 10^{-4} \text{M}, \ \text{pH} = 2.0, 100 \ \text{mL sample solutions}, \ \text{N}_2 \text{ flow rate} = 10 \ \text{cc min}^{-1} \).
Time, Min.

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FIGURE XIV

FLOTATION OF Ir(III): INFLUENCE OF SURFACTANT SECONDARY CHAIN LENGTH

Initial Flotation Conditions: [Ir(III)] = 5x10^{-5}M, [Surfactant] = 2x10^{-4}M, pH = 2.0, 100 mL sample solutions, N_2 flow rate = 10 cc min^{-1}.
FIGURE XV

PERCENTAGE OF EACH METAL FLOATED
AS A FUNCTION OF SECONDARY CHAIN LENGTH

Initial Flotation Conditions: 
\[ [\text{Metal}] = 5 \times 10^{-5} \text{M}, \]
\[ [\text{Surfactant}] = 2 \times 10^{-4} \text{M}, \text{pH} = 2.0, \text{100 mL sample solution}, \text{N}_2 \text{ flow rate} = 10 \text{ cc min}^{-1}. \]

Flotation time = 2 hours.
Flotation with surfactants of the type $C_{16}H_{33}NR_3Br$
hours. The maximum percentage of each metal floated with each surfactant is given in Table IV.

Examination of Figure XV and Table IV indicates that the selectivity sequence is Au(III) > Pd(II), Pt(IV), Ir(IV) > Ir(III) > Rh(III) at steady state for all surfactants except C_{16}H_{33}NH_{3}^{+}. It may be seen that as surfactant secondary chain length increases the percentage of Pd(II), Ir(IV), Pt(IV) and Au(III) also increases; however, the percentage of Ir(III) and Rh(III) floated decreases. An increase in the percentage floated with increasing secondary chain length was expected as in the primary chain length studies because of the increase in surface activity discussed before.

The decrease in percentage floated for the Rh(III) and Ir(III) as the secondary chain length is increased is thought to be the result of the charge and size of their chlorocomplexes. The RhCl_{6}^{3-} and IrCl_{6}^{3-} ions are comparable in size to the tetramethylammonium ion. Thus as the length of the secondary chains is increased, the size of the quaternary ammonium ion becomes very large relative to the platinum metal chlorocomplexes. Pd(II), Pt(IV) and Ir(IV) require only a 2:1 mole ratio of surfactant to metal for flotation. However, the Rh(III) and Ir(III) require a 3:1 mole ratio. Apparently, the crowding of three large ammonium groups around the small anions is sterically unfavorable and leads to a reduction in flotation.
TABLE IV

MAXIMUM PERCENTAGE OF EACH OF THE PLATINUM METALS FLOATED WITH SURFACTANTS OF VARYING SECONDARY CHAIN LENGTH

<table>
<thead>
<tr>
<th>R'</th>
<th>Surfactant</th>
<th>Pd(II)</th>
<th>Ir(IV)</th>
<th>Pt(IV)</th>
<th>Au(III)</th>
<th>Rh(III)</th>
<th>Ir(III)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>HAC</td>
<td>88</td>
<td>82</td>
<td>23</td>
<td>20</td>
<td>30</td>
<td>62</td>
</tr>
<tr>
<td>CH₃</td>
<td>HTMAB</td>
<td>98</td>
<td>84</td>
<td>82</td>
<td>95</td>
<td>25</td>
<td>55</td>
</tr>
<tr>
<td>C₂H₅</td>
<td>HTEAB</td>
<td>98</td>
<td>89</td>
<td>85</td>
<td>97</td>
<td>10</td>
<td>38</td>
</tr>
<tr>
<td>C₃H₇</td>
<td>HTPAB</td>
<td>100</td>
<td>99</td>
<td>98</td>
<td>100</td>
<td>0</td>
<td>18</td>
</tr>
<tr>
<td>C₄H₉</td>
<td>HTBAB</td>
<td>99</td>
<td>99</td>
<td>100</td>
<td>100</td>
<td>0</td>
<td>5</td>
</tr>
</tbody>
</table>
The most important observation that may be made from Figure XV is that separations of the Ir(III) and Rh(III) from the other metals are possible because of the low percentage floated with increasing secondary chain length. Separations based on these observations will be fully discussed in Chapter IV.

C. INFLUENCE OF INITIAL HCl CONCENTRATION

Previous studies (26,94) have shown that the distribution coefficients obtained for the platinum metals for anion exchange resins vary greatly as the HCl concentration is varied. Since the functional groups of both the surfactants in these studies and the anion exchange resins are of the quaternary ammonium type, and also as it is of interest to recover the platinum metals from acidic solution, it was decided to continue the survey of the flotation properties of the platinum group metals by floating each metal from solutions initially containing 0.01 to 3.0 M HCl.

Although the maximum percentage floated for each metal differs with each surfactant, the observed trends are the same. Therefore, only the data obtained for each metal with the surfactants HTMAB and HTPAB are presented. The data for HTMAB were chosen so that a comparison could be made between the anion exchange data and ion flotation data. The data for HTPAB were chosen because of separations utilizing this surfactant presented in Chapter IV.
Rate of removal curves obtained for each metal with HTMAB and selected HCl concentrations are shown in Figures XVI to XXI. The rate of removal curves for HTMAB are representative of similar behavior for each metal with the other surfactants. The percentage floated for each metal after two hours with HTPAB is plotted versus HCl concentration in Figure XXII. Finally, the maximum percentage floated for each metal with HTMAB and HTPAB from solutions of various HCl concentrations is given in Tables V and VI, respectively.

Gold(III) forms a colloidal precipitate upon mixing with either HTMAB or HTPAB over the range of HCl concentrations studied. Platinum(IV) and Ir(IV) form precipitates with both surfactants in HCl concentrations up to 1.0 M, but are not precipitated by HTPAB in greater concentrations of HCl. Palladium(II), Ir(III) and Rh(III) do not form precipitates with HTPAB and form precipitates with HTMAB only in dilute HCl (less than 0.05 M).

The rate of removal curves presented in Figures XVI to XXI indicate that as the HCl concentration increases the time for attaining steady state also increases. It may be seen in Figure XXII that for all the metals except Au(III) there is a decrease in the relative amounts floated as the HCl concentration increases. These trends were expected because an increase in the concentration of HCl increases the Cl\(^-\) competition with the anionic metal chlorocomplexes for the cationic surfactant. In addition, due to the
FIGURE XVI

FLOTATION OF Pd(II): INFLUENCE OF HCl CONCENTRATION

Initial Floation Conditions: \([\text{Pd(II)}] = 5 \times 10^{-5}, \ [\text{Surfactant}] = 2 \times 10^{-4} \text{M}, 100 \text{ mL sample solutions}\)

\(N_2\) flow rate = 10 cc min\(^{-1}\).
FIGURE XVII

FLOTATION OF Ir(IV): INFLUENCE OF HCl CONCENTRATION

Initial Flotation Conditions:  [Ir(IV)] = 5x10⁻⁵ M, [Surfactant] = 2x10⁻⁴ M, 100 mL sample solutions, \(N_2\) flow rate = 10 cc min⁻¹.

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FIGURE XVIII

FLOTATION OF Pt(IV): INFLUENCE OF HCl CONCENTRATION

Initial Flotation Conditions: \([\text{Pt(IV)}] = 5 \times 10^{-5} \text{M},\]
\([\text{Surfactant}] = 2 \times 10^{-4} \text{M},\) 100 mL sample solutions,
\(\text{N}_2 \text{ flow rate} = 10 \text{ cc min}^{-1}.\)
FIGURE XIX

FLOTATION OF Au(III): INFLUENCE OF HCl CONCENTRATION

Initial Flotation Conditions: [Au(III)] = 5x10^{-5} M,
[Surfactant] = 2x10^{-4} M, 100 mL sample solutions
N_2 flow rate = 10 cc min^{-1}.

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Au(III) : HTMA
in HCl solution

\[
\frac{C_t}{C_0}
\]

Time, Min

\[
\begin{cases}
0.1 M \text{ HCl} \\
0.5 M \text{ HCl} \\
3.0 M \text{ HCl}
\end{cases}
\]
FIGURE XX

FLOTATION OF Rh(III): INFLUENCE OF HCl CONCENTRATION

Initial Flotation Conditions: [Rh(III)] = 5x10^{-5}, [Surfactant] = 2x10^{-4} M, 100 mL sample solutions, N\textsubscript{2} flow rate = 10 cc min\textsuperscript{-1}.

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FIGURE XXI

FLOTATION OF Ir(III): INFLUENCE OF HCl CONCENTRATION

Initial Flotation Conditions: \([\text{Ir(III)}] = 5 \times 10^{-5} \text{M},\]
\([\text{Surfactant}] = 2 \times 10^{-4} \text{M}, 100 \text{ mL sample solutions},\]
\(N_2\) flow rate = 10 cc min \(^{-1}\).
0.5 M HCl

1.0 M HCl

0.5 M HCl

0.1 M HCl

0.01 M HCl

Ir(III) : HTMAB
in HCl solution

Time, Min
FIGURE XXII

PERCENTAGE OF EACH METAL FLOATED

AS A FUNCTION OF HCl CONCENTRATION

Initial Flotation Conditions: [Metal] = 5 x 10^{-5} M,
[Surfactant] = 2x10^{-4} M, 100 mL sample solutions,
N₂ flow rate = 10 cc min⁻¹. Flotation time = 2 hours.

Pd(II), Ir(IV), Pt(IV), Au(III) and Ir(III)
floated with HTPAB. Rh(III) floated with HTKAB.
Concentration of HCl, molarity

Influence of HCl Concentration on Flotation
<table>
<thead>
<tr>
<th>HCl M</th>
<th>Pd(II)</th>
<th>Ir(IV)</th>
<th>Pt(IV)</th>
<th>Au(III)</th>
<th>Rh(III)</th>
<th>Ir(III)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.01</td>
<td>98</td>
<td>84</td>
<td>82</td>
<td>95</td>
<td>25</td>
<td>55</td>
</tr>
<tr>
<td>0.10</td>
<td>97</td>
<td>83</td>
<td>82</td>
<td>--</td>
<td>20</td>
<td>28</td>
</tr>
<tr>
<td>0.50</td>
<td>84</td>
<td>81</td>
<td>82</td>
<td>93</td>
<td>0</td>
<td>10</td>
</tr>
<tr>
<td>1.00</td>
<td>36</td>
<td>75</td>
<td>75</td>
<td>96</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>2.00</td>
<td>2</td>
<td>71</td>
<td>70</td>
<td>97</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>3.00</td>
<td>0</td>
<td>65</td>
<td>63</td>
<td>95</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>
TABLE VI

MAXIMUM PERCENTAGE OF EACH OF THE PLATINUM METALS FLOATED WITH HTPAB FROM SOLUTIONS OF VARYING HCl CONCENTRATION

Initial Flotation Conditions: \([\text{Metal}] = 5 \times 10^{-5} \text{M}, \ [\text{HTPAB}] = 2 \times 10^{-6} \text{M}\).

Flotation time = 2 hours for Pd(II), Ir(IV), Pt(IV), Rh(III) and Ir(III).

Flotation time = 4 hours for Au(III).

<table>
<thead>
<tr>
<th>HCl (M)</th>
<th>Pd(II)</th>
<th>Ir(IV)</th>
<th>Pt(IV)</th>
<th>Au(III)</th>
<th>Rh(III)</th>
<th>Ir(III)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.01</td>
<td>100</td>
<td>99</td>
<td>90</td>
<td>100</td>
<td>~0</td>
<td>18</td>
</tr>
<tr>
<td>0.10</td>
<td>97</td>
<td>98</td>
<td>98</td>
<td>50</td>
<td>0</td>
<td>10</td>
</tr>
<tr>
<td>0.50</td>
<td>85</td>
<td>97</td>
<td>95</td>
<td>90</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>1.00</td>
<td>40</td>
<td>95</td>
<td>90</td>
<td>95</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>2.00</td>
<td>~3</td>
<td>85</td>
<td>79</td>
<td>97</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>3.00</td>
<td>0</td>
<td>78</td>
<td>60</td>
<td>98</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>
increase in $\text{H}^+$ concentration the anionic chlorocomplexes may form the soluble molecular acids, such as $\text{H}_2\text{PdCl}_4^-$, which are not floated. As far as could be determined, the $K_a$ values for the platinum group metal chlorocomplexes have not been published.

In Chapter I, the enrichment ratio was discussed. The enrichment ratio is defined as the concentration of solute in the foam divided by the concentration in bulk solution after steady state is attained (45). The enrichment ratio indicates the extent to which flotation is useful for concentrating solutes from dilute solutions and the comparison of enrichment ratios for different solutes floated under the same conditions indicates the feasibility of flotation as a separation method.

The enrichment ratios obtained for the flotation of each metal from 100 mL of solution (various HCl concentrations) into 0.2 mL of foam with HTMAB are shown in Table VII. The selectivity sequence in 0.01 M HCl is Au(III) > Pd(II), Pt(IV), Ir(IV) > Ir(III) > Rh(III). Furthermore, a significant depression of flotation for Pd(II), Ir(III) and Rh(III) is indicated for increasing HCl concentrations and it may be seen that single stage batch flotation processes may be used for separations by the simple adjustment of HCl concentration (Chapter IV).

It is also of interest to compare the ion flotation enrichment ratios to anion exchange distribution coefficients.
### TABLE VII

**ENRICHMENT RATIOS FOR THE PLATINUM METALS**

Surfactant: $C_{16}H_{33}N(CH_3)_3Br$

Foam Volume: 0.2 mL

Bulk Volume: 100 mL

<table>
<thead>
<tr>
<th>M, HCl</th>
<th>Au(III)</th>
<th>Ir(IV)</th>
<th>Pt(IV)</th>
<th>Pd(II)</th>
<th>Ir(III)</th>
<th>Rh(III)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.01</td>
<td>9500</td>
<td>2625</td>
<td>3667</td>
<td>24500</td>
<td>587</td>
<td>167</td>
</tr>
<tr>
<td>0.1</td>
<td>2278</td>
<td>2845</td>
<td>6650</td>
<td>78</td>
<td>50</td>
<td></td>
</tr>
<tr>
<td>0.5</td>
<td>9500</td>
<td>1995</td>
<td>2613</td>
<td>2450</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>1.0</td>
<td>9500</td>
<td>1775</td>
<td>1886</td>
<td>321</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>2.0</td>
<td>9500</td>
<td>1575</td>
<td>1173</td>
<td>10</td>
<td>1</td>
<td>1</td>
</tr>
</tbody>
</table>

Selectivity Sequence: Au(III) > Pt(IV), Ir(IV), Pd(II) > Ir(III) > Rh(III)
The data of Kraus and Nelson (94) and Berman and McBryde (26) for the distribution coefficients of the chlorocomplexes of the platinum metals for an anion exchanger resin of the type \( \text{RN(CH}_3\text{)}_3\text{Cl} \) are thus presented in Table VIII. These coefficients are obtained by stirring a weighed amount of resin in a solution with the metal of interest. The equilibrium concentration of metal is then determined and the distribution coefficients are reported as moles of solute per kilogram of resin divided by the molar concentration of the solution.

The selectivity sequence which has been observed for the flotation of the platinum group metals indicates that the flotation of the singly charged anion > doubly charged anions > triply charged anions. This sequence is in disagreement with the prediction of Pinfold (40) that as the ionic charge increases, the fraction floated would also increase. Likewise, the selectivity of ion exchange resins for various ions has also been shown to increase with ionic charge (95). However, the distribution coefficients of the anion exchange resin indicate the same selectivity sequence found for ion flotation Table (VIII). It is therefore reasonable to assume that the forces which cause the strong binding of \( \text{Au(III)}, \text{Pd(II)}, \text{Ir(IV)} \) and \( \text{Pt(IV)} \) to the anion exchange resin would also cause strong binding to the quaternary ammonium surfactants. The strong binding in turn, results in greater flotation values for these metals.
**TABLE VIII**

**ANION EXCHANGE DISTRIBUTION COEFFICIENTS FOR THE PLATINUM GROUP METALS**

[Data from McBryde (22) and Kraus (24,94)]

Resin: \(\text{RN(CH}_3\text{)}_3\text{Cl}\)

<table>
<thead>
<tr>
<th>(M, \text{ HCl})</th>
<th>(\text{Au(III)})</th>
<th>(\text{Ir(IV)})</th>
<th>(\text{Pt(IV)})</th>
<th>(\text{Pd(II)})</th>
<th>(\text{Ir(III)})</th>
<th>(\text{Rh(III)})</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>(10^7)</td>
<td>18600</td>
<td>44000</td>
<td>45000</td>
<td>1050</td>
<td>15</td>
</tr>
<tr>
<td>0.5</td>
<td>(10^7)</td>
<td>59000</td>
<td>27000</td>
<td>15000</td>
<td>350</td>
<td>12</td>
</tr>
<tr>
<td>1.0</td>
<td>(10^6)</td>
<td>32000</td>
<td>20000</td>
<td>4300</td>
<td>60</td>
<td>10</td>
</tr>
<tr>
<td>2.0</td>
<td>(10^6)</td>
<td>18000</td>
<td>4000</td>
<td>400</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

*Selectivity Sequence: Au(III) > Ir(IV) > Pt(IV) > Pd(II) > Ir(III) > Rh(III)*
D. INFLUENCE OF INITIAL NaCl CONCENTRATION

It is also of interest to determine the influence of chloride ion concentration on the flotation of the platinum metals in neutral or weakly acidic solution, without the presence of large concentrations of H⁺. Therefore, the flotation properties of each metal from solutions containing various concentrations of NaCl were studied.

The data for the flotation of each platinum metal with the surfactants HTMAB and HTPAB from various NaCl solutions are again presented as representative of the trends observed with all of the other surfactants. The rate of removal curves are not presented because they are similar to those shown before. About 60 minutes were required for each of the metals to reach steady state except Au(III) which required about 3.5 hours.

Collodial precipitates were observed when Au(III), Pt(IV) and Ir(IV) were mixed with either HTMAB or HTPAB regardless of the concentration of NaCl in the solution. Palladium(II), Ir(III) and Rh(III) did not form precipitates with HTPAB and were precipitated by HTMAB only in dilute NaCl solution (<0.05 M).

The percentage of each metal floated with HTMAB and HTPAB after two hours is plotted versus initial NaCl concentration in Figure XXIII. The maximum percentage of each metal floated with HTMAB and HTPAB from solutions of various NaCl concentrations is given in Tables IX and X, respectively.
FIGURE XXIII
PERCENTAGE OF EACH METAL FLOATED
AS A FUNCTION OF NaCl CONCENTRATION

Initial Flotation Conditions: [Metal] = 5x10^{-5} M, [Surfactant] = 5x10^{-5} M, pH = 2.0, 100 mL sample solutions, N_2 flow rate = 10 cc min^{-1}.

Flotation time = 2 hours.

Pd(II), Pt(IV), Ir(IV), Au(III) and Ir(III) floated with HTPAB. Rh(III) floated with HTMAB.
Influence of NaCl Concentration on Flotation
TABLE IX

MAXIMUM PERCENTAGE OF EACH OF THE PLATINUM METALS FLOATED WITH HTMAB FROM SOLUTIONS OF VARYING NaCl CONCENTRATION

Initial Flotation Conditions: [Metal] = 5x10^{-5} M, [HTMAB] = 2x10^{-4} M, pH = 2.0.
Flotation time = 2 hours for Pd(II), Ir(IV), Pt(IV), Rh(III) and Ir(III).
Flotation time = 4 hours for Au(III).

<table>
<thead>
<tr>
<th>M, NaCl</th>
<th>Pd(II)</th>
<th>Ir(IV)</th>
<th>Pt(IV)</th>
<th>Au(III)</th>
<th>Rh(III)</th>
<th>Ir(III)</th>
</tr>
</thead>
<tbody>
<tr>
<td>--</td>
<td>98</td>
<td>84</td>
<td>82</td>
<td>95</td>
<td>25</td>
<td>55</td>
</tr>
<tr>
<td>0.50</td>
<td>76</td>
<td>81</td>
<td>76</td>
<td>94</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>1.00</td>
<td>56</td>
<td>76</td>
<td>70</td>
<td>96</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>2.00</td>
<td>18</td>
<td>74</td>
<td>66</td>
<td>96</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>3.00</td>
<td>6</td>
<td>73</td>
<td>62</td>
<td>95</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>
Maximum Percentage of Each of the Platinum Metals Floated with HTPAB from Solutions of Varying NaCl Concentration

Initial Flotation Conditions: [Metal] = 5 \times 10^{-5} \text{M}, [HTPAB] = 2 \times 10^{-4} \text{M}, \text{pH} = 2.0.

Flotation time = 2 hours for Pd(II), Ir(IV), Pt(IV), Rh(III) and Ir(III).

Flotation time = 4 hours for Au(III).

<table>
<thead>
<tr>
<th>M, NaCl</th>
<th>Pd(II)</th>
<th>Ir(IV)</th>
<th>Pt(IV)</th>
<th>Au(III)</th>
<th>Rh(III)</th>
<th>Ir(III)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>100</td>
<td>99</td>
<td>98</td>
<td>100</td>
<td>0</td>
<td>18</td>
</tr>
<tr>
<td>0.50</td>
<td>78</td>
<td>99</td>
<td>95</td>
<td>98</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>1.00</td>
<td>58</td>
<td>98</td>
<td>92</td>
<td>98</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>2.00</td>
<td>20</td>
<td>97</td>
<td>88</td>
<td>99</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>3.00</td>
<td>10</td>
<td>96</td>
<td>78</td>
<td>97</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>
The flotation for all the metals except Au(III) decreases with increasing NaCl concentration, but the reduction is not as great as with HCl. The flotation of Pd(II), Rh(III) and Ir(III) is again significantly reduced. These effects are also thought to be due to Cl\(^-\) competition for the surfactant. Separation procedures based on these observations will be discussed in Chapter IV.

A significant decrease in the percentage of Pt(IV), Ir(IV) and Au(III) floated is observed as the NaCl concentration is increased from 0 to about 0.3 M. The percentage floated then increases as the NaCl concentration is raised to 0.5 M. Observations similar to these were explained in a previous flotation study by Walkowiak and Bartecki (72) who indicated that colloidal precipitates do not float to a great extent when dispersed in solutions of dilute chloride concentrations. As the chloride concentration is increased, the precipitates agglomerate and are more readily floated. The trend was not observed in the HCl studies for Pt(IV) or Ir(IV), but was observed for the flotation of Au(III).

E. INFLUENCE OF INITIAL SURFACTANT CONCENTRATION

In the previous studies, the initial metal chlorocomplex concentrations were each held to fixed values of 5 \(\times\) 10\(^{-5}\) M and enough of each surfactant was added to give 2 \(\times\) 10\(^{-4}\) M solutions. The amount of surfactant was therefore in excess of the stoichiometric amount required to float 100% of each
metal. It was important, however, to ascertain if the surfactant concentration had to be rigidly fixed in order to provide optimum flotation conditions for each of the metals. It was expected that concentrations of surfactant less than the stoichiometric amount would not completely float all the colligend. Previous research (40) had indicated that surfactant concentrations greater than the stoichiometric amount in certain cases depressed flotation, possibly because of the formation of micelles or because of the "coating" of colloidal sublate in the solution with a layer of the excess surfactant with the surfactant hydrophilic groups oriented into the solution.

The percentage floated after two hours for Pt(IV), Ir(IV), Ir(III) and Pd(II) with HTPAB and for Au(III) with PTMAB and Rh(III) with HTMAB are plotted versus surfactant concentration in Figure XXIV. It is important to note that increasing the concentrations of surfactant above the stoichiometric amount does not decrease the percentage floated for any of the platinum group metals as might be expected from previous studies.

As the surfactant concentration is increased from zero to the stoichiometric amount for Pd(II), Pt(IV), Ir(IV) and Au(III), the amount floated also increases. The percentage floated reached 100% only after the predicted stoichiometric concentration is exceeded. The Ir(III) and
FIGURE XXIV

PERCENTAGE OF EACH METAL FLOATED AS A FUNCTION OF INITIAL SURFACTANT CONCENTRATION

Initial Flotation Conditions: [Metal] = 5x10^{-5}M, pH = 2.0, 100 mL sample solutions, N₂ flow rate = 10 cc min⁻¹. Flotation time = 2 hours.

Pd(II), Ir(IV), Pt(IV) and Ir(III) floated with HTPAB. Au(III) floated with PTMAB. Rh(III) floated with HTMAB.
Concentration of Surfactant $\times 10^4$

- $M = 5 \times 10^{-5}$ M

- $\text{Pd (II)}$
- $\text{Pt (IV)}$
- $\text{Ir (III)}$
- $\text{Rh (III)}$

Peidol $\times \%$

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Rh(III) are not completely floated by increasing the concentration of surfactant.

The useful conclusion from these studies is that the surfactant concentration does not need to be rigidly controlled to ensure complete flotation of Pt(IV), Ir(IV), Au(III) and Pd(II) as long as there is an excess of the stoichiometric amount. However, a large excess of the concentration of surfactant over the stoichiometric amount produces large volumes of foam which decrease the usefulness of ion flotation as a concentrating procedure. The data in Table XI for the flotation of Ir(IV) with HTPAB exemplify this observation. It may be seen that the concentration of the iridium in the foam is significantly reduced as the surfactant concentration is increased.

F. INFLUENCE OF INITIAL METAL CHLOROCOMPLEX CONCENTRATION

The studies of the variation of surfactant concentration with fixed metal concentrations were supplemented by a study of fixed surfactant concentrations and varying initial metal chlorocomplex concentrations. The maximum percentage of each metal floated with varying initial concentrations of Ir(IV), Pt(IV) and Pd(II) with HTPAB and of Au(III) with PTMAB is shown in Figure XXV.

All the metals are floated quantitatively from the solution as long as there is an excess of surfactant. These results further support the conclusion that the initial concentration of neither the colligend nor the surfactant needs to be rigidly controlled as long as an excess of
TABLE XI
FLOTATION OF Ir(IV) FROM SOLUTIONS OF VARYING HTPAB CONCENTRATION

Initial Flotation Conditions: [Ir(IV)] = 5x10^{-5} M, pH = 2.0, sample solution volume = 100 mL. Flotation time = 1 hour.

<table>
<thead>
<tr>
<th>Concentration of HTPAB, Mx10^{-4}</th>
<th>Mole Ratio(S/M)</th>
<th>Percent Floated</th>
<th>Volume of Liquid in Foam, mL</th>
<th>Concentration in Foam, Mx10^{-2}</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>1</td>
<td>45</td>
<td>0.1</td>
<td>2.25</td>
</tr>
<tr>
<td>1.0</td>
<td>2</td>
<td>95</td>
<td>0.2</td>
<td>2.38</td>
</tr>
<tr>
<td>1.5</td>
<td>3</td>
<td>100</td>
<td>0.2</td>
<td>2.50</td>
</tr>
<tr>
<td>2.0</td>
<td>4</td>
<td>100</td>
<td>0.4</td>
<td>1.25</td>
</tr>
<tr>
<td>4.0</td>
<td>8</td>
<td>100</td>
<td>1.2</td>
<td>0.42</td>
</tr>
<tr>
<td>7.0</td>
<td>14</td>
<td>100</td>
<td>2.3</td>
<td>0.22</td>
</tr>
<tr>
<td>10.0</td>
<td>20</td>
<td>100</td>
<td>3.5</td>
<td>0.14</td>
</tr>
</tbody>
</table>
FIGURE XXV

PERCENTAGE OF Pd(II), Pt(IV), Ir(IV) AND Au(III) FLOATED AS A FUNCTION OF INITIAL METAL CHLOROCOMPLEX CONCENTRATION

Initial Flotation Conditions: [Surfactant] = 1x10^{-3} M, pH = 2.0, 100 mL sample solutions, \( N_2 \) flow rate = 10 cc min^{-1}. Flotation time = 2 hours. Pd(II), Pt(IV) and Ir(IV) floated with HTPAB. Au(III) floated with PTMAB.

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surfactant is added.

G. RECOVERY OF THE PLATINUM METALS VIA MODIFIED SOLVENT SUBLATION

It is of interest to recover the platinum metals from industrial effluents and other sources. Often, the concentrations of these metals are very low and a concentrating step is required before further processing. Ion exchange resins may be used to concentrate these metals, but the recovery of the metals from the resin is a time consuming, difficult task involving Soxhlet extractions with HCl for long periods (26).

The studies discussed above in Sections 1 through 6 indicate that Pt(IV), Pd(II), Ir(IV) and Au(III) can be quantitatively floated from dilute solutions with certain surfactants. Conditions for quantitatively floating Rh(III) and Ir(III) were not found. In order to quantitatively recover the metals, procedures were investigated for efficiently collecting the sublates from the foam.

The most obvious means for recovering the sublate after the metal is completely floated from the solution is to simply scrape the foam from above the solution with a spatula. This procedure is very inefficient as much of the sublate adheres to the sides of the flotation column or is redispersed into the solution.

Another means of recovering the sublate is to drain the bulk liquid from below the foam after which the foam
and the entire column is washed with acetone into a collecting vessel. Although the sublate can be recovered quantitatively with this procedure, some of the original liquid is also collected. If the original liquid contains unwanted impurities, the sublate will be contaminated.

The best method of collecting the pure sublate is by solvent sublation. Solvent sublation is the method that involves the addition of an organic solvent to the top of the aqueous solution before flotation. As the gas bubbles rise, the sublate is carried directly into the organic solvent where it dissolves. Thus there is little or no contamination of the sublate from impurities present in the aqueous solution, as long as these impurities are insoluble in the chosen organic liquid.

A reduction in the percentage metal floated is observed when solvent sublation is used to collect metals from solutions of varying Cl\(^-\) concentration. The reduction in the percentage of Ir(IV) floated with HTPAB from solutions of varying concentrations of NaCl when n-butyl acetate is used as the organic solvent is shown in Figure XXVI.

The reduction in flotation is thought to be due to the surfactant dissolving in the organic layer with chloride as its counterion. For the Ir(IV) flotation the exchange reaction is:

\[
2(SCl) + \text{IrCl}_6^{2-} \rightarrow S_2\text{IrCl}_6 + 2\text{Cl}^-
\]

where \(S = \) surfactant cation.
FIGURE XXVI
PERCENTAGE OF Ir(IV) COLLECTED
BY DIRECT SOLVENT SUBLATION
AS A FUNCTION OF NaCl CONCENTRATION
Initial Flotation Conditions: [Ir(IV)] = 5x10^{-5}M,
[HTPAB] = 2x10^{-4}M, pH = 2.0, 100 mL sample
solutions, solvent = n-butyl acetate (25 mL).
Flotation time = 1 hours.
In the usual ion flotation process, the surfactant is present in the foam in both the chloride and sublate forms; the relative amounts of which are based on the distribution coefficient. As the foam collapses, the sublate remains as a solid while the surfactant returns to the solution, equilibrium is shifted as the free surfactant reacts with more colligend and thus, more Ir(IV) is floated. However, when an organic layer is above the aqueous solution, both forms are dissolved and the surfactant does not return to the solution for further flotation. The trend of reduction in flotation with increasing chloride concentration is therefore due to a shift in the equilibrium toward the left.

To overcome this problem, yet still employ the advantages of solvent sublation, the recovery of the several metals was accomplished by quantitatively floating them without the presence of an organic solvent. After flotation was completed, an organic solvent was added which caused the foam to collapse. Flotation was then resumed to float any sublate that was redispersed into the solution by the addition of the organic solvent. The organic and aqueous layers were then carefully separated.

The platinum metals were recovered by evaporating the organic solvent. The residue was wet ashed with nitric acid, fumed with HCl and filtered. The time for the entire procedure is no more than four hours and, usually, is much less. The data in Table XII indicate that ion flotation and
**TABLE XII**

**RECOVERY OF Au(III), Ir(IV), Pd(II) AND Pt(IV) BY ION FLOTATION**

Initial Flotation Conditions: [Metal] = 2.5x10⁻⁴ M, [Surfactant] = 6x10⁻⁴ M, 0.1 M HCl, 100 mL sample solutions. Flotation time = 1 hour. Recovery by modified solvent sublation in n-butyl acetate

<table>
<thead>
<tr>
<th>Metal</th>
<th>Surfactant</th>
<th>mg Added</th>
<th>mg Recovered</th>
<th>Percent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au(III)</td>
<td>PTMAB</td>
<td>4.924</td>
<td>4.913</td>
<td>99.8</td>
</tr>
<tr>
<td>Au(III)</td>
<td>PTMAB</td>
<td>4.924</td>
<td>4.920</td>
<td>99.9</td>
</tr>
<tr>
<td>Au(III)</td>
<td>PTMAB</td>
<td>4.924</td>
<td>4.890</td>
<td>99.3</td>
</tr>
<tr>
<td>Ir(IV)</td>
<td>HTPAB</td>
<td>4.805</td>
<td>4.796</td>
<td>99.8</td>
</tr>
<tr>
<td>Ir(IV)</td>
<td>HTPAB</td>
<td>4.805</td>
<td>4.810</td>
<td>100.2</td>
</tr>
<tr>
<td>Ir(IV)</td>
<td>HTPAB</td>
<td>4.805</td>
<td>4.798</td>
<td>99.8</td>
</tr>
<tr>
<td>Pd(II)</td>
<td>HTPAB</td>
<td>2.660</td>
<td>2.645</td>
<td>99.4</td>
</tr>
<tr>
<td>Pd(II)</td>
<td>HTPAB</td>
<td>2.660</td>
<td>2.615</td>
<td>98.3</td>
</tr>
<tr>
<td>Pd(II)</td>
<td>HTPAB</td>
<td>2.660</td>
<td>2.639</td>
<td>99.2</td>
</tr>
<tr>
<td>Pt(IV)</td>
<td>HTPAB</td>
<td>4.877</td>
<td>4.791</td>
<td>98.2</td>
</tr>
<tr>
<td>Pt(IV)</td>
<td>HTPAB</td>
<td>4.877</td>
<td>4.803</td>
<td>98.5</td>
</tr>
<tr>
<td>Pt(IV)</td>
<td>HTPAB</td>
<td>4.877</td>
<td>4.862</td>
<td>99.7</td>
</tr>
</tbody>
</table>
solvent sublation can yield quantitative recoveries of Pt(IV), Ir(IV), Au(III) and Pd(II). The process is an improvement over conventional ion exchange methods as it is less time consuming, simpler and does not require expensive equipment or chemicals.
CHAPTER IV
ION FLOTATION SEPARATIONS OF SOME PLATINUM GROUP METAL MIXTURES

Conditions were noted in the foregoing studies in which some of the platinum metals were floated while others remained in the bulk solution, unfloated. It seemed possible, therefore, that some of the platinum metals could be separated from each other by simply adjusting the initial solution conditions of mixtures so that one metal was preferentially floated. The preferentially floated metal then was recovered by a modified solvent sublation technique. It was thought also that quantitative separations could be obtained.

Conditions were not found whereby all of the platinum metals studied could be separated from each other, but several important binary separations were developed. These binary separations include iridium from rhodium, platinum from iridium and platinum from palladium. Each of these three mixtures is isolated at various points during the classical (industrial) separation of the platinum group metals. It will be shown that ion flotation separations offer some improvement over other methods of separating these mixtures and may have practical significance in the group separation scheme.

A. THE SEPARATION OF IRIDIUM AND RHODIUM

The separation of iridium and rhodium has been described
as the most difficult step in the refinement of the platinum group metals (2). The classical separation of these metals involves fusion with NaHSO₄ in which rhodium forms a water soluble sulphato complex, while iridium remains as an insoluble residue. The rhodium complex is dissolved in water and separated from the iridium by filtration. The separation is time consuming and inefficient.

Another method of separating rhodium and iridium is with anion exchange chromatography. Rhodium and iridium metals are dissolved in aqua regia after fusion with Na₂O₂ to give Rh(III) and Ir(IV). Fuming the residue with HCl and dissolution in aqueous HCl yields the RhCl₆³⁻ and IrCl₆²⁻. These complexes are separated by anion exchange chromatography more efficiently than by the NaHSO₄ fusion method. However, the procedure suffers from the time consuming necessity of having to Soxhlet extract the resin for six to eight hours with HCl in order to recover the Ir(IV) (22).

Thus, the traditional methods for separating these metals have disadvantages. It was thought that ion flotation separations of rhodium and iridium would be less time consuming and more efficient than the traditional methods of separation.

Methods for separating Rh(III) and Ir(IV) are presented below that are based on the observations made for single metal flotation studies. It was shown that flotation
decreases for Rh(III) as the surfactant secondary chain length increases; i.e., the percentage floated for Rh(III) with HTMAB > HTEAB > HTPAB. It is seen that Ir(IV) can be floated quantitatively with HTPAB while Rh(III) remains in the bulk solution, unfloated. Furthermore, an increase in the solution Cl\(^{-}\) concentration, either as HCl or NaCl, was shown to reduce the percentage of Rh(III) floated with HTMAB and HTEAB to zero, while the flotation of Ir(IV) is unaffected. Therefore, mixtures of Ir(IV) and Rh(III) with several surfactants and in solutions of varying Cl\(^{-}\) concentration were prepared for flotation separation.

Solutions were prepared for flotation separation in the same manner as solutions in the single metal studies except that mixtures of Rh(III) and Ir(IV) were added. Ce(IV) was also added in order to avoid Ir(IV) reduction by the surfactant. The modified solvent sublation procedure was used to recover the Ir(IV) from the foam. The solvent used was n-butyl acetate because it has a low miscibility with water, has a low boiling point and can be flash evaporated from the collected sublate.

The total separation time is three to four hours including the time required for solution preparation, flotation and recovery of Ir(IV) by wet ashing the sublate. The separation time does not include the time required to prepare the Rh(III) and Ir(IV) complexes from the metals.
Data obtained for the flotation separation indicated that the flotation properties of Ir(IV) and Rh(III) were not changed as a result of mixing the metals. The data for the recovery of Rh(III) and Ir(IV) from solutions containing various concentrations of HCl and for the surfactants HTMAB, HTEAB, HTPAB and HTBAB are shown in Table XIII. Data are presented in Table XIV for the recoveries of Rh(III) and Ir(IV) from solutions of various NaCl concentrations. The data indicate that ion flotation is an efficient method for separating iridium and rhodium after the chlorocomplexes of these metals have been prepared by traditional methods.

It is suggested that the ion flotation separation of rhodium and iridium is an improvement over the conventional ion exchange chromatographic separation because of the savings in time. Furthermore, the Soxhlet extraction step involving the recovery of Ir(IV) from the anion exchange resins results in the destruction of the resin. Even though the surfactants are also destroyed in the ion flotation recovery process, they are considerable less expensive than anion exchange resins. Finally, it is possible that ion flotation may be more easily applied in a large scale industrial process than the ion exchange method.

B. THE SEPARATION OF PLATINUM AND IRIDIUM

A second separation of importance in the refinement of the platinum group metals is that of platinum from iridium.
**TABLE XIII**

**RECOVERY DATA FOR THE SEPARATION OF Ir(IV) AND Rh(III)**

Initial Separation Conditions: $[\text{Ir(IV)}] = [\text{Rh(III)}] = 5 \times 10^{-5}$ m, $[\text{Surfactant}] = 2 \times 10^{-4}$ m, 100 mL sample solutions. Flotation time = 1 hour. Recovery: Ir(IV) in n-butyl acetate, Rh(III) from residual aqueous solution. 0.5 mL of 1% Ce(IV) solution added to prevent Ir(IV) reduction.

<table>
<thead>
<tr>
<th>Surfactant</th>
<th>$\text{M, HCl}$</th>
<th>mg Rh Added</th>
<th>mg Rh Recovered</th>
<th>% Rh Recovered</th>
<th>mg Ir Added</th>
<th>mg Ir Recovered</th>
<th>% Ir Recovered</th>
</tr>
</thead>
<tbody>
<tr>
<td>HTMAB</td>
<td>0.01</td>
<td>0.515</td>
<td>0.378</td>
<td>73</td>
<td>0.961</td>
<td>0.809</td>
<td>84</td>
</tr>
<tr>
<td></td>
<td>0.10</td>
<td>0.515</td>
<td>0.421</td>
<td>82</td>
<td>0.961</td>
<td>0.797</td>
<td>83</td>
</tr>
<tr>
<td></td>
<td>0.50</td>
<td>0.515</td>
<td>0.520</td>
<td>101</td>
<td>0.961</td>
<td>0.780</td>
<td>81</td>
</tr>
<tr>
<td></td>
<td>1.00</td>
<td>0.515</td>
<td>0.516</td>
<td>100</td>
<td>0.961</td>
<td>0.760</td>
<td>79</td>
</tr>
<tr>
<td></td>
<td>2.00</td>
<td>0.515</td>
<td>0.524</td>
<td>102</td>
<td>0.961</td>
<td>0.693</td>
<td>72</td>
</tr>
<tr>
<td></td>
<td>3.00</td>
<td>0.515</td>
<td>0.505</td>
<td>98</td>
<td>0.961</td>
<td>0.595</td>
<td>62</td>
</tr>
<tr>
<td>HTEAB</td>
<td>0.01</td>
<td>0.515</td>
<td>0.468</td>
<td>91</td>
<td>0.961</td>
<td>0.865</td>
<td>90</td>
</tr>
<tr>
<td>HTPAB</td>
<td>0.01</td>
<td>0.515</td>
<td>0.510</td>
<td>99</td>
<td>0.961</td>
<td>0.953</td>
<td>99</td>
</tr>
<tr>
<td></td>
<td>0.10</td>
<td>0.515</td>
<td>0.511</td>
<td>99</td>
<td>0.961</td>
<td>0.935</td>
<td>97</td>
</tr>
<tr>
<td></td>
<td>0.50</td>
<td>0.515</td>
<td>0.515</td>
<td>100</td>
<td>0.961</td>
<td>0.910</td>
<td>95</td>
</tr>
<tr>
<td></td>
<td>1.00</td>
<td>0.515</td>
<td>0.526</td>
<td>102</td>
<td>0.961</td>
<td>0.894</td>
<td>93</td>
</tr>
<tr>
<td></td>
<td>2.00</td>
<td>0.515</td>
<td>0.514</td>
<td>100</td>
<td>0.961</td>
<td>0.788</td>
<td>82</td>
</tr>
<tr>
<td></td>
<td>3.00</td>
<td>0.515</td>
<td>0.509</td>
<td>99</td>
<td>0.961</td>
<td>0.692</td>
<td>72</td>
</tr>
<tr>
<td>HTBAB</td>
<td>0.01</td>
<td>0.515</td>
<td>0.506</td>
<td>98</td>
<td>0.961</td>
<td>0.973</td>
<td>101</td>
</tr>
<tr>
<td></td>
<td>0.10</td>
<td>0.515</td>
<td>0.510</td>
<td>99</td>
<td>0.961</td>
<td>0.940</td>
<td>98</td>
</tr>
<tr>
<td></td>
<td>1.00</td>
<td>0.515</td>
<td>0.520</td>
<td>101</td>
<td>0.961</td>
<td>0.837</td>
<td>87</td>
</tr>
<tr>
<td></td>
<td>3.00</td>
<td>0.515</td>
<td>0.514</td>
<td>100</td>
<td>0.961</td>
<td>0.750</td>
<td>78</td>
</tr>
</tbody>
</table>
**TABLE XIV**

**RECOVERY DATA FOR THE SEPARATION OF Ir(IV) AND Rh(III)**

Initial Separation Conditions: \([\text{Ir(IV)}] = [\text{Rh(III)}] = 5 \times 10^{-5} \text{M}, [\text{Surfactant}] = 2 \times 10^{-4} \text{M}, \text{pH} = 2.0, 100 \text{ mL sample solutions. Flotation time} = 1 \text{ hour. Recovery: Ir(IV) in n-butyl acetate, Rh(III)}\) from residual aqueous solution. 0.5 mL of 1% Ce(IV) solution added to prevent Ir(IV) reduction.

<table>
<thead>
<tr>
<th>Surfactant</th>
<th>M NaCl Added</th>
<th>mg Rh Recovered</th>
<th>% Rh Recovered</th>
<th>mg Ir Added</th>
<th>mg Ir Recovered</th>
<th>% Ir Recovered</th>
</tr>
</thead>
<tbody>
<tr>
<td>HTMAB</td>
<td>--</td>
<td>0.515</td>
<td>0.361</td>
<td>70</td>
<td>0.961</td>
<td>0.806</td>
</tr>
<tr>
<td></td>
<td>0.10</td>
<td>0.515</td>
<td>0.438</td>
<td>85</td>
<td>0.961</td>
<td>0.705</td>
</tr>
<tr>
<td></td>
<td>0.50</td>
<td>0.515</td>
<td>0.515</td>
<td>100</td>
<td>0.961</td>
<td>0.778</td>
</tr>
<tr>
<td></td>
<td>1.00</td>
<td>0.515</td>
<td>0.515</td>
<td>100</td>
<td>0.961</td>
<td>0.750</td>
</tr>
<tr>
<td></td>
<td>2.00</td>
<td>0.515</td>
<td>0.516</td>
<td>101</td>
<td>0.961</td>
<td>0.759</td>
</tr>
<tr>
<td></td>
<td>3.00</td>
<td>0.515</td>
<td>0.514</td>
<td>99</td>
<td>0.961</td>
<td>0.721</td>
</tr>
<tr>
<td>HTEAB</td>
<td>--</td>
<td>0.515</td>
<td>0.458</td>
<td>89</td>
<td>0.961</td>
<td>0.875</td>
</tr>
<tr>
<td>HTPAB</td>
<td>--</td>
<td>0.515</td>
<td>0.510</td>
<td>99</td>
<td>0.961</td>
<td>0.951</td>
</tr>
<tr>
<td></td>
<td>0.10</td>
<td>0.515</td>
<td>0.505</td>
<td>98</td>
<td>0.961</td>
<td>0.700</td>
</tr>
<tr>
<td></td>
<td>0.50</td>
<td>0.515</td>
<td>0.510</td>
<td>99</td>
<td>0.961</td>
<td>0.942</td>
</tr>
<tr>
<td></td>
<td>1.00</td>
<td>0.515</td>
<td>0.520</td>
<td>101</td>
<td>0.961</td>
<td>0.932</td>
</tr>
<tr>
<td></td>
<td>2.00</td>
<td>0.515</td>
<td>0.506</td>
<td>98</td>
<td>0.961</td>
<td>0.914</td>
</tr>
<tr>
<td></td>
<td>3.00</td>
<td>0.515</td>
<td>0.514</td>
<td>100</td>
<td>0.961</td>
<td>0.922</td>
</tr>
<tr>
<td>HTBAB</td>
<td>--</td>
<td>0.515</td>
<td>0.519</td>
<td>101</td>
<td>0.961</td>
<td>0.971</td>
</tr>
<tr>
<td></td>
<td>0.10</td>
<td>0.515</td>
<td>0.505</td>
<td>98</td>
<td>0.961</td>
<td>0.814</td>
</tr>
<tr>
<td></td>
<td>1.00</td>
<td>0.515</td>
<td>0.501</td>
<td>97</td>
<td>0.961</td>
<td>0.951</td>
</tr>
<tr>
<td></td>
<td>3.00</td>
<td>0.515</td>
<td>0.525</td>
<td>102</td>
<td>0.961</td>
<td>0.932</td>
</tr>
</tbody>
</table>
Both of these metals exist in the +4 oxidation state after dissolution in aqueous HCl as the PtCl$_6^{2-}$ and IrCl$_6^{2-}$. The chemical properties of the +4 oxidation state for each metal are very similar; thus separations are difficult. However, in certain cases the Ir(IV) may be readily reduced to the Ir(III), while Pt(IV) is not reduced under the same conditions. The difference in chemical properties of the chlorocomplex anions of Ir(III) and Pt(IV) may be utilized to separate the two metals.

The ion exchange separation of platinum and iridium developed by Busch et al., (27) utilizes the difference in the distribution coefficients of PtCl$_6^{2-}$ and IrCl$_6^{3-}$ for anion exchange resins to separate the metals. In their procedure, Ir(IV) is reduced to Ir(III) with hydroxylamine, while the platinum remains as Pt(IV). Although the separation is quick, about 3% of the platinum elutes with the Ir(III).

It was indicated in Chapter III that the surfactant HTBAB quantitatively floats Pt(IV). Furthermore, only a small amount of Ir(III) is floated by HTBAB. It was also shown that increasing the HCl concentration reduces the percentage of Ir(III) floated to zero. Therefore it was suggested that a flotation separation of Ir(III) and Pt(IV) could be achieved with HTBAB in 0.1 M HCl. It was also thought that other surfactants could be used for a separation of these metals in more concentrated HCl solutions.
For the flotation separation of platinum and iridium, the reduction step of Busch's anion exchange procedure was used as a step in the flotation procedure. Prior to the preparation of sample solutions for flotation, the Pt(IV) and Ir(IV) aliquots were mixed, heated with 0.25 mL of 10% hydroxylamine hydrochloride to reduce the Ir(IV) to Ir(III) and cooled before mixing with the surfactant. The Pt(IV) was recovered by the modified solvent sublation procedure with n-butyl acetate. Data are presented in Table XV for the separations of Pt(IV) and Ir(III) with various surfactants from solutions of various HCl concentrations. Similar data are presented in Table XVI for the separations of Pt(IV) and Ir(III) from solutions containing various concentrations of NaCl. These data indicate that ion flotation may be used for the quantitative separation of platinum and iridium.

C. THE SEPARATION OF PLATINUM AND PALLADIUM

In most industrial and laboratory procedures for the separation of the platinum group metals, the platinum and palladium pair are isolated from the other platinum group metals (2). The classical method of separating these metals involves the precipitation of PtCl$_6^{2-}$ as its ammonium salt, (NH$_4$)$_2$PtCl$_6$. The separation is incomplete, however, as the salt has a water solubility of about 0.7 grams per 100 mL. Therefore an improved method for separating palladium and platinum would be very beneficial.
RECOVERY DATA FOR THE SEPARATION OF Pt(IV) AND Ir(III)

Initial Separation Conditions: \([\text{Pt(IV)}] = [\text{Ir(III)}] = 5\times10^{-5}\text{M}, [\text{Surfactant}] = 2\times10^{-4}\text{M}\), 100 mL sample solutions. Flotation time = 1 hour. Recovery: Pt(IV) in n-butyl acetate, Ir(III) from residual aqueous solution. 0.25 mL of 10% \(\text{NH}_3\cdot\text{OH}\cdot\text{HCl}\) solution added to reduce Ir(IV) to Ir(III).

<table>
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<tr>
<th>Surfactant</th>
<th>M, HCl</th>
<th>mg Ir Added</th>
<th>mg Ir Recovered</th>
<th>% Ir Recovered</th>
<th>mg Pt Added</th>
<th>mg Pt Recovered</th>
<th>% Pt Recovered</th>
</tr>
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<tbody>
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TABLE XVI

RECOVERY DATA FOR THE SEPARATION OF Pt(IV) AND Ir(III)

Initial Separation Conditions: [Pt(IV)] = [Ir(III)] = 5x10^{-5} M, [Surfactant] = 2x10^{-4} M, pH = 2.0, 100 mL sample solutions. Flotation time = 1 hour. Recovery: Pt(IV) in n-butyl acetate, Ir(III) from residual aqueous solution. 0.25 mL of 10% NH_{3}OH•HCl solution added to reduce Ir(IV) to Ir(III).

<table>
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<th>M, NaCl</th>
<th>mg Ir Added</th>
<th>mg Ir Recovered</th>
<th>% Ir Recovered</th>
<th>mg Pt Added</th>
<th>mg Pt Recovered</th>
<th>% Pt Recovered</th>
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<td>0.975</td>
<td>0.915</td>
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</table>
An examination of the accumulated flotation data for Pd(II) and Pt(IV) indicates that a partial separation of the two metals is possible by flotation from HCl solutions. Separations are possible because the percentage of Pd(II) decreases to zero as the HCl concentration is increased. Unfortunately, the amount of platinum floated also decreases, which indicates that a quantitative separation cannot be obtained. However, the process may be useful as pure platinum can be recovered from the foam.

The data in Table XVII indicate the result of the flotation separation of Pd(II) and Pt(IV) with various surfactants from solutions of various concentrations of HCl. The platinum was recovered by the modified solvent sublation procedure and, in some cases, is free of palladium.

Since the flotation studies of PdCl$_4^{2-}$ and PtCl$_6^{2-}$ did not yield information that lead to the development of satisfactory separations methods for the pair, a second approach was attempted. In the presence of ammonia, palladium very readily forms the ammine as indicated by the reaction:

\[
PdCl_4^{2-} + 4NH_3 \rightarrow \text{Pd(NH}_3)_4^{2+} + 4Cl^{-}
\]

Under the same conditions, Pt(IV) does not form an ammine complex but it can be precipitated as (NH$_4$)$_2$PtCl$_6$. Fortunately, the initial 5 x 10$^{-5}$ M concentration of the PtCl$_6^{2-}$ is much smaller than the amount necessary to exceed
# TABLE XVII

RECOVERY DATA FOR THE PARTIAL SEPARATION OF Pd(II) AND Pt(IV)

Initial Separation Conditions: [Pt(IV)] = [Pd(II)] = 5x10^-5 M, [Surfactant] = 2x10^-4 M, 100 mL sample solutions. Flotation time = 1 hour. Recovery: Pt(IV) in n-butyl acetate, Pd(II) from residual aqueous solution.

<table>
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<th>Surfactant</th>
<th>M, HCl</th>
<th>mg Pd Added</th>
<th>mg Pd Recovered</th>
<th>% Pd Recovered</th>
<th>mg Pt Added</th>
<th>mg Pt Recovered</th>
<th>% Pt Recovered</th>
</tr>
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<tbody>
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<td>0.017</td>
<td>3</td>
<td>0.975</td>
<td>0.762</td>
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<td>0.752</td>
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<td>0.733</td>
<td>75</td>
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<td>0.644</td>
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the solubility limits of (NH\textsubscript{4})\textsubscript{2}PtCl\textsubscript{6}. Since the ammine complex of palladium is cationic, it was thought that it would not be floated by the quaternary ammonium surfactants used in these studies, while the PtCl\textsubscript{6}^{2-} would continue to be floated as before.

Since the palladium ammine complex readily forms when ammonia is added in excess without heating, only a slight modification in the flotation procedure was necessary. Prior to the dilution of the Pt(IV)/Pd(II) sample prepared for flotation separation, an aliquot of 1 M ammonium hydroxide was added to the sample solutions. The Pd(NH\textsubscript{3})\textsubscript{4}^{2+} was completely formed within 10 minutes.

Due to the addition of the ammonia, the final solutions are basic. In basic solution, the following reaction occurs:

\[
\text{PtCl}_6^{2-} + \text{OH}^- \rightarrow \text{Pt(OH)}_x(\text{Cl})_{6-x}^{2-} \rightarrow \text{Pt(OH)}_6^{2-} + 6\text{Cl}^- \]

Although all the hydrolysis products are anionic, they are not efficiently floated by the cationic surfactants. However, hydrolysis does not constitute a major problem for this separation because the rate of the reaction is slow (96).

Furthermore, if the amount of ammonia added is too small to convert completely all of the chloropalladate to the complex ammine, then the insoluble Vauquelin's salt, [Pd(NH\textsubscript{3})\textsubscript{4}][PdCl\textsubscript{4}], forms. It was found that enough excess ammonia must be added to give the final solution a pH of 10 or
greater to avoid the precipitation of Vauquelin's salt.

The data for the separation of Pd(II) and Pt(IV) with several surfactants and solutions of various ammonia concentration are given in Table XVIII. It is seen that a quantitative separation is achieved in 0.01 M ammonia. Larger concentrations of ammonia decrease the efficiency of the separation.

D. OTHER SEPARATION PROCEDURES

Other binary separations may be developed in the same manner as the separations discussed above. It is likely, for instance, that Au(III), Pt(IV) or Pd(II) can be separated from Rh(III) just as Ir(IV) was separated from Rh(III) by using the surfactant HTPAB, which floats the Au(III), Pt(IV) and Pd(II) but does not float Rh(III). Furthermore, Au(III) may be separated from Rh(III), Ir(III) or Pd(II) by the appropriate adjustment of the initial HCl concentration, which depresses the flotation of Rh(III), Ir(III) and Pd(II) to zero, while the flotation of Au(IV) is unaffected. Although it is interesting that these metals could be separated using ion flotation, the separations are not of major significance and therefore are not discussed in detail.
TABLE XVIII

RECOVERY DATA FOR THE SEPARATION OF Pt(IV) AND Pd(II)

Initial Separation Conditions: [Pt(IV)] = [Pd(II)] = $5 \times 10^{-5}$ M, [Surfactant] = $2 \times 10^{-4}$ M, 100 mL sample solutions. Flotation time = 1 hour. Recovery: Pt(IV) in n-butyl acetate, Pd(II) from residual aqueous solution. Aqueous ammonia added after mixing metals and surfactant.

<table>
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<th>Surfactant</th>
<th>$\text{M}, \text{NH}_3$</th>
<th>mg Pd Added</th>
<th>mg Pd Recovered</th>
<th>% Pd Recovered</th>
<th>mg Pt Added</th>
<th>mg Pt Recovered</th>
<th>% Pt Recovered</th>
</tr>
</thead>
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CHAPTER V
CONCLUSIONS AND SUGGESTIONS FOR FUTURE WORK

The objectives of this work were to study the ion flotation properties of the platinum group metals, to develop methods for the quantitative recovery of the platinum metals from dilute solution by ion flotation and to investigate the feasibility of ion flotation for the group separation. A summary of the results of this work is now presented along with suggestions for future work.

Cationic surfactants of the quaternary ammonium type were used to float the anionic chlorocomplexes of Pd(II), Pt(IV), Ir(IV), Au(III), Rh(III) and Ir(III) from aqueous solutions. A number of parameters were investigated to determine their influence on the rate and efficiency of the flotation for each of the metals. These parameters were the surfactant primary chain length, the surfactant secondary chain length, the initial surfactant concentration, the initial metal chlorocomplex ion concentration, the initial HCl concentration and the initial NaCl concentration. It was found that most of the surfactants float each of the metal chlorocomplexes. It was also found that the time required to reach steady state and the maximum percentage floated for each of the platinum metals varied significantly for surfactants of various primary and secondary chain lengths. Furthermore, it was found that regardless of which surfactant was used for
flotation, the percentage of Pd(II), Ir(III) and Rh(III) floated greatly decreased as the initial HCl or NaCl concentration was increased, and that the percentage of Pt(IV), Ir(IV) and Au(III) floated decreased to a lesser extent.

An ion flotation selectivity sequence of Au(III) > Ir(IV), Pt(IV), Pd(II) > Ir(III) > Rh(III) was established for flotation with quaternary ammonium surfactants. The flotation trends were verified by comparing previously determined anion exchange distribution coefficients to the enrichment ratios obtained for the ion flotation studies.

Only the chlorocomplexes of the platinum metals were studied in this work. It would be of interest to extend the flotation studies of the platinum metals to other complexes which are readily prepared such as the bromides, iodides, thiocyanates, ammines, etc. since chloride is undesirable in some studies. With some ligands the platinum metals form cationic complexes, thus anionic surfactants could be used for flotation which may be more useful in an industrial process because anionic surfactants are more stable in aqueous solution and are less expensive than the quaternary ammonium surfactants.

The usefulness of ion flotation for recovering the platinum metals from dilute solutions was also investigated. It was shown that palladium, platinum, iridium and gold can be quantitatively recovered from solutions containing less than 10 ppm of each of these metals. However,
conditions were not found for the quantitative flotation of rhodium, thus further studies need to be done.

One approach to find conditions for efficiently floating rhodium is to evaluate previously obtained ion exchange chromatography data to find the optimum conditions for recovering rhodium from aqueous solutions. Rhodium should be efficiently floated with surfactants having the same functional group as the ion exchange resin, from a solution having the same composition as the eluant and by utilizing the same chemical form of rhodium. For example, the nitrito complex, \( \text{Rh(NO}_2\text{)}_6^{3-} \), has been recovered by anion exchange chromatography; therefore this complex should be efficiently floated with quaternary ammonium surfactants.

Finally, the primary goal of this work was to develop a new method for the separation of the platinum group metals. Although conditions were not found for a single stage, batch ion flotation separation of all the metals studied, separations of iridium from rhodium, platinum from iridium and platinum from palladium were developed and were shown to be improvements over other separations methods for these mixtures.

Ion flotation separations have not yet been used for separating mixtures of the platinum metals containing more than two of the metals. It is possible that ternary mixtures of the platinum group metals could be separated.
by the methods discussed in this work in a two step flotation process. For example, a mixture of platinum, iridium and rhodium could be separated by floating Pt(IV) and Ir(IV) from Rh(III) with HTBAB. The floated platinum and iridium could then be recovered and separated after reducing the iridium to Ir(III) by again floating the Pt(IV) from the solution with HTBAB.

Furthermore, it also seems possible that a quaternary mixture of the platinum group metals could be separated in a three step process. For example, a mixture of platinum, iridium, rhodium and palladium could be separated as described above except that an additional step is required wherein the palladium is converted to the cationic ammine complex and the platinum is separated by flotation with HTBAB.

Multistep flotations of the platinum metals may be useful for separating the platinum metals but are possibly too time consuming to be useful since the floated metals would have to be chemically treated prior to each subsequent flotation step. Furthermore, the flotation behavior of the platinum metals in multimetal mixtures has not yet been established. However, it does seem possible that future investigations of the ion flotation behavior of the platinum metals may lead to conditions whereby a group separation scheme could be developed.


3. Ibid., pp. 413-487.

4. Ibid., p. 215.

5. Ibid., p. 457.


20. F. E. Beamish, Talanta, 14, 991 (1967).


30. Ibid., p. 12.
31. Ibid., pp. 45-70.
32. Ibid., p. 95.
33. Ibid., p. 87.
34. Ibid., pp. 90-126.
40. Ibid., pp. 53-74.
52. B. L. Karger and D. G. Devivio, Separ. Sci., 3, 393 (1968).
69. Jacobelli-Turi, Ibid., p. 163.
73. Walkowiak, Ibid., p. 209.
85. Ibid., pp. 769-774.
86. Ibid., pp. 503-505.
89. N. Kember and R. Wells, Analyst (London), 80, 735 (1955).
VITA

Daniel Murphy Downey was born on November 14, 1952 in Winchester in the Shenandoah Valley of Virginia. After attending elementary school and high school in Strasburg, Virginia, he received a Bachelor of Science degree cum laude from Madison College in Harrisonburg, Virginia, in May, 1975.

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Major Field: Analytical Chemistry

Title of Thesis: Ion Flotation Studies and Separation Procedures for the Platinum Group Metals.

Approved:

Eugene W. Berg
Major Professor and Chairman

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Date of Examination:

April 24, 1980