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Synergic solvent extraction and thermal studies of fluorinated Beta-diketone-organophosphorus adduct complexes of lanthanide and related elements

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SYNERGIC SOLVENT EXTRACTION AND THERMAL
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SYNERGIC SOLVENT EXTRACTION AND THERMAL STUDIES OF FLUORINATED
BETA-DIKETONE-ORGANOPHOSPHORUS ADDUCT COMPLEXES OF LANTHANIDE
AND RELATED ELEMENTS

by

James Winfield Mitchell

A Dissertation Submitted to the
Graduate Faculty in Partial Fulfillment of
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DOCTOR OF PHILOSOPHY

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1970

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INTRODUCTION

Solvent extraction and gas chromatography have proven to be very successful techniques for quantitative separation and determination of many types of compounds. While the former has been well established as a universal tool for both organic and inorganic separations, the latter has been primarily used for organic applications. Recent investigations (80) however, have amply demonstrated the utility of gas chromatography for inorganic analysis. Although both techniques provide excellent analytical capabilities, a greater analytical potential for separation and determination of inorganic materials would be produced by a combination of the two techniques. The combination of the resolution capabilities of gas chromatography and the specificity of solvent extraction should considerably broaden the scope of practical analysis of cationic mixtures.

During a recent study at the Ames Laboratory a mixture of hexafluoroacetylacetone (HHFA) and tri-n-butylphosphate (TBP) in cyclohexane was used for the first time as a gas chromatographic reagent for the lanthanide elements (19). This initial work included a broad spectrum of studies designed to assess the potential of mixed-ligand chelates for inorganic gas chromatography. The successful gas chromatography (GC)

of all rare earth (R.E.) chelates of HHFA-TBP was demonstrated. Additional studies of this system and more detailed investigations of other synergic systems were required for an adequate evaluation of the capabilities of this new approach for effecting quantitative gas chromatographic analysis of cations. A comprehensive study of the solvent extraction of mixed systems capable of forming volatile complexes with the rare earths was essential since this technique can be conveniently used for preparation of chromatographable species and the synergic systems most likely to be suitable for this purpose have not yet been fully investigated.

In order to be compatible with subsequent gas chromatographic analysis an extraction system must satisfy several requirements during the extraction process:

- 1) The species to be chromatographed must be rapidly prepared and quantitatively transferred to the organic phase.
- 2) The extraction reaction should produce a specie in the organic phase of constant composition. Thus at appropriately chosen conditions the properties of the synergic system should allow precise control of the formation of the extracted complex.
- 3) The extraction system should be selective for R.E., thereby allowing interfering substances to be previously

extracted or to remain in the aqueous phase.

In order to obtain pertinent information it was necessary to conduct a fundamental solvent extraction study of those fluorinated β -diketones most extensively employed as gas chromatographic reagents. Primary considerations during this research were focused on several aspects of the liquid-liquid extraction system. The major areas of concern included: a comparison of the extraction properties of various mixed systems for lanthanide and related elements; a survey of the separation capabilities of these systems; the establishment of extraction conditions compatible with subsequent gas chromatographic analysis; a determination of the composition of the extracted species and an evaluation of the important equilibrium or stability constants involved in the extraction processes.

For this research the β -diketones trifluoroacetylacetone (HTFA)¹, hexafluoroacetylacetone (HHFA) and 8,8,8,7,7,6,6-heptafluoro-2,2-dimethyl-3,5-octanedione (HFOD) were selected since these ligands have been most extensively employed in gas chromatographic studies and are known to form volatile and thermally stable β -ketoenolates. The compounds, 1,1,1,

¹See Appendix for structures of β -diketones.

5,5,6,6,7,7,7-decafluoro-2,4-heptanedione (HFHD) and 1,1,1,2,2,6,6,7,7,8,8,8-dodecafluoro-3,5-octanedione (HDODEFOD) were also studied.

The organophosphorus compounds tri-n-butylphosphate (TBP) and the new fluoro-organophosphorus adducts, tri(2,2,2-trifluoroethyl)phosphate (TFEP) and tri(3,3,3,2,2-pentafluoropropyl)phosphate (PFPP) were used as donors.

Cations were extracted from aqueous chloride-acetate media since these anions are not likely to participate in the formation of extractable species (47,48). The buffer action of this media was also advantageous. The trivalent rare earths Nd, Eu and Tm were primarily studied because of their atomic numbers and the suitable properties of available radioisotopes.

The organic diluents, benzene and cyclohexane were utilized respectively in normal diketone and synergic extractions because large distribution ratios were found in these solvents.

The influence of adduct formation on relative trends in volatility and thermal stability of rare earth and uranium chelates was studied by thermoanalytical techniques.

REVIEW OF THE LITERATURE

The emphasis of this research is primarily focused on aspects of the solvent extraction of the rare earths and related elements by aliphatic fluorinated β -diketones alone and in synergic systems in combination with TBP. Influences of adduct formation on volatility and thermal stability of rare earth and uranium chelates was also studied. This review will therefore be restricted to the literature reporting investigations related to the extraction properties of fluorinated and other aliphatic β -diketones which possess the potential to form volatile chelate complexes. Studies on the separation of cations, synergic extractions and the volatility of fluorinated and non-fluorinated chelates are reviewed.

Fluorinated β -Diketones in Chelating Extraction Systems

Following the preparation and early studies of chelate complexes of the parent β -diketone, acetylacetone (HAA), investigations by numerous workers were simultaneously undertaken to probe further into the nature of the rather unusual properties of metal acetylacetonates. The appreciable vapor pressure of these chelates stimulated sublimation, vaporization (12) and gas chromatography studies (80). The high

solubility of the acetylacetonates in organic solvents led to extensive studies on the liquid-liquid extraction of cations by this reagent. Several investigators were instrumental in the introduction of new fluorinated β -diketones. Reid and Calvin (89) synthesized a series of β -diketones and studied the effects of the trifluoromethyl group. They characterized compounds with the general formula $\text{RCOCH}_2\text{COCF}_3$, where R is the methyl, ethyl, isobutyl and n-hexyl groups, and also prepared the corresponding copper chelates. The inductive effect of the trifluoromethyl group produced a significant increase in the acidity of the enol forms of these diketones. Park, Brown and Lacher (84) prepared the following β -diketones: $\text{CF}_3\text{COCH}_2\text{COCH}_3$, $\text{CF}_3\text{CF}_2\text{COCH}_2\text{COCH}_3$, $\text{CF}_3(\text{CF}_2)_2\text{COCH}_2\text{COCH}_3$ and $\text{CF}_3(\text{CF}_2)_3\text{COCH}_2\text{COCH}_3$. The physical properties, infrared spectra, and the percentage of enolization of these compounds were measured. The percentage of enolization of the fluorinated β -diketones was found to be greater than that of the corresponding hydrocarbon derivatives. These workers attributed this phenomena to a greater tendency of the fluorinated compounds to form hydrogen bonds. Schweitzer and Benson's (96) studies on keto-enol tautomeric equilibrium showed steric effects of the R groups to be an additional contributing factor. Barkley and Levine (5) prepared a series of

β -diketones containing the perfluoromethyl and perfluoro-n-propyl groups. During the period, 1950-60, the interest in the exploitation of solvent extraction techniques for separation of cations grew at an exponential rate. The search for other diketones with extraction properties more favorable than those of acetylacetone resulted in the introduction of fluorinated β -diketones as solvent extractants.

Several classified and patented procedures for the purification and separation of by-product materials from nuclear reactors were developed. In this area thenoyltrifluoroacetone (HTTA) was the most extensively used fluorinated β -diketone. Although this ligand has been widely used for many successful separations by solvent extraction, its chelates are not readily volatile or easily chromatographed. Thus, only a limited amount of the literature on this ligand has been included in this review. The interested reader is referred to the books of Morrison and Freiser (80) and Stary (118) for more information about the extraction properties of HTTA.

A patent issued to Winkle (129) granted rights for the separation of Pa(V) from U(VI), Th(IV) and the rare earths by extraction with HTTA, benzoyltrifluoroacetone (HBTA) or HTFA. Th(IV) and Pa(V) were simultaneously extracted at $\text{pH} > 0.9$.

Crandall and Thomas (28) obtained rights for the separation of Zr(IV) from a mixture containing niobium, rare earths and alkaline earths by extraction with HTFA, HTTA and HBTA. Separation of ^{95}Zr from uranium fission products was claimed.

The patent of Werner et al. (128) included rights for the use of methyl, propyl, isovaleryl, heptyl, benzyl and 2-thenyl derivatives of trifluoroacetylacetone for the separation of Am(III) from La(III) and Th(IV). Monofluoroacetylacetone and difluoroacetylacetone were also included. Am(III) was separated from La(III) by extraction of the former with a solution of HTFA in benzene at pH 2.5-4.0. A separation of Am(III) from Th(IV) could be similarly accomplished at any pH between 0.2 and 3. Calvin (21) reported distribution ratios for the extraction of Pu(III) into benzene solutions containing 0.41 M HTFA, 0.33 M HBTA, 0.2 M 3-methyltrifluoroacetylacetone, 0.22 M trifluoropropionylacetone, 0.27 M 3-methyltrifluoropropionylacetone or 0.12 M isovaleryltrifluoroacetone. The respective distribution ratios for extractions from 0.5 M HNO_3 were 11.5, 400, 0.0, >52, 0.0, and 37. Hagemann (44) claimed rights to the use of HTTA or HTFA dissolved in benzene for the extractive separation of Ac(III) from Ra(II) and decay products. By a selective back-extraction into an aqueous phase, Ac(III) was separated from Th(IV)

and other impurities that were simultaneously extracted into the organic phase. Crandal et al. (29) studied the extraction of Pu(IV) by a solution of HTFA in benzene. Rates of extraction of Pu(IV) and the acid- and base-catalyzed hydrolysis of HTFA were studied.

Schultz and Larsen (95) investigated the extraction of Zr and Hf by solutions of HTFA in benzene. In the extraction of Zr and Hf from hydrochloric acid solutions the distribution ratios followed a fourth power dependence on the β -diketone concentration. Evidence for polymerization and complexation of the metals by chloride in the aqueous phase was presented. Zr was successfully separated from hafnium by extracting 0.2 M HCl solutions of the cations with a solution of HTFA in benzene. In two extractions, the mole % of Hf in a Zr-Hf mixture was reduced from 1.56 to less than 0.1-0.05 with a 6.9% yield of the original Zr. In six extractions, the mole % of Hf in a Zr-Hf mixture was increased from 7.5 to 99.98 mole % with a 37.6% yield of the original Hf. Huffman et al. (55) also studied the extraction of Zr and Hf by fluorinated β -diketones. Distribution ratios and equilibrium constants for the extraction of these cations from 4 M perchloric acid with various combinations of fluorinated β -diketones and organic solvents were determined. The separation factors,

K_{Zr}/K_{Hf} , were: HTTA in benzene, 25; HTTA in 1,2-dichlorobenzene, 16; HBTA in benzene, 18; isovaleryltrifluoroacetone in benzene, 13 and in hexane, 13.

An extensive study of the extraction of cations with 1,1,1-trifluoro-7-methyl-2,4-octanedione (FMOD) was conducted by Schweitzer and Willis (98). The distribution of Th(IV), In(III), Co(II), Pm(III), Zn(II), Sc(III), Ag(I), Hg(II), and Tl(I) was studied by using FMOD and the corresponding hydrocarbon compound as a chelating solvent. Distribution curves for cations extracted by the former were shifted to lower pH values than those of the latter. These workers discussed theoretical considerations and compared the advantages and disadvantages of extraction with chelating solvents and chelating agents dissolved in diluents.

After Biermann and co-workers (15) accomplished the first successful gas chromatography of metal chelates of acetylacetone, other investigators eagerly pursued research in the area of inorganic gas chromatography. Their needs for convenient methods of preparing metal chelate complexes further stimulated interest in the extraction properties of β -diketones. The discovery of the improved thermal stability and gas chromatographability of chelates of the β -diketones, HTFA and HHFA led to studies on the solvent extraction and gas

chromatography of chelates of these compounds. Morie and Sweet (78) separated milligram and microgram quantities of Fe(III) from Al(III) by extraction with a 0.25 M solution of HTFA in benzene. The pH range 1.5 to 2.0 was suitable for this separation. Both cations were simultaneously extracted in the pH range, 4.5 to 6.5, and were quantitatively measured by gas chromatography. These workers (77) also analyzed mixtures of aluminum, gallium and indium by solvent extraction and gas chromatography of the HTFA chelates. Extraction with 0.25 M solutions of HTFA in benzene removed 99.9% of these cations from aqueous solutions initially as concentrated as 8.0×10^{-3} M. The pH range 4.5 to 6.5 was suitable for quantitative extractions. Thallium(III) was poorly extracted under the previously mentioned conditions. Scribner, Treat and Weis (101) extracted copper, iron and aluminum from aqueous acetate solutions with 0.10 M solutions of HTFA in chloroform. At equilibrium pH values between 4.5 and 5.5, 99.0% Cu(II), 99.7% Al(III) and 99.9% Fe(III) were removed from aqueous phases containing initially 0.5 millimole of the metal ion. Under these conditions Mn(II), Ni(II), Zn(II) and Mg(II) were poorly extracted (1 to 3%). Separation of Fe(III) from Cu(II) and from Al(III) could be accomplished by control of the pH and by complexation with EDTA in the aqueous phase.

The poor extraction of Cr(III) also permitted the separation of Fe(III), Cu(II) and Al(III) from this cation.

Scribner, Borchers and Treat (99) studied the extraction of beryllium by HTFA and HHFA. Benzene solutions 0.25 M in HTFA quantitatively extracted Be(II) in the pH region 5.0 to 7.0. Similar extractions with HHFA removed only 23% of the Be(II). Data showing the percentage of extraction of the divalent cations, Ni, Co, Zn, Cd, Mn, Mg, Pb and Cu and La(III) by 0.25 M solutions of HTFA in butanol were also reported.

Stokely (119) conducted a comprehensive study of the extraction of Al(III), Be(II), Zr(IV) and Hf(IV) by 1.0 M solutions of HTFA and HHFA in benzene. The large concentrations of reagent which were necessary to achieve extraction of macro quantities of these metals in reasonable equilibration times resulted in volume changes upon equilibration. Al(III) was quantitatively extracted from a 0.063 M aqueous phase into a 1.0 M solution of HTFA in benzene in sixty minutes at equilibrium pH values between 4.0 and 7.0. Beryllium was similarly extracted from a 0.11 M aqueous solution over the range pH 2.5 to 6.0. During one-hour extractions of 2.82 M HCl solutions which were also initially 0.21 M in Zr(IV) or 0.010 M in Hf, 94.2% and 92.5% of the cations were extracted into the organic phase, respectively. Hexafluoroacetylacetone was

shown to be an extremely poor extractant for cations. Aluminum was less than 5% extracted by 1.0 M solutions of this reagent over the pH range 1.8 to 8.6. For beryllium, no extraction was observed at pH 7.5 or 6.5 after equilibration with a 1.0 M solution of HHFA in benzene for one hour. No extraction of Zr(IV) and Hf(IV) was observed. The poor extraction of metals by HHFA was attributed to a weak tendency for chelate formation.

Rare earth chelates of 2,2,6,6-tetramethyl-3,5-heptanedione (HTHD) have been successfully gas chromatographed without apparent decomposition (34). Sweet and Parlett (120) undertook a study to determine whether the lanthanides could be quantitatively extracted with this reagent as the chelating solvent. Although Pr(III), Sm(III), Eu(III), Gd(III) and Tb(III) were quantitatively extracted from aqueous solutions 0.1 M in tetraethyl ammonium perchlorate over the pH range 7 to 12.5, an equilibration time of 5 hours was necessary. It was also evident from their discussion that the practical utility of this reagent for the quantitative extraction of small amounts of rare earths would be limited by the irreversible formation of hydroxide complexes in the aqueous phase.

Synergic Solvent Extraction with Fluorinated β -Diketones
and Neutral Donor Molecules

The most recent era in extraction chemistry was begun by the discovery that small concentrations of neutral extractants in the presence of acidic ligands produced a large enhancement in the extraction of cations into organic solvents. Cuninghame and co-workers (30) found that the extraction of rare earths by HTTA was greatly enhanced by small amounts of tri-n-butylphosphate. Blake et al. (16) described this phenomena as a synergic solvent extraction. The term synergism as employed by these workers denoted the cooperative action of two or more extractants to produce an overall effect which is greater than the sum of the individual actions of the components when used alone.

Many types of synergic systems have been studied since 1959. The literature has grown so voluminous that a complete review of this topic can not be considered practical. Those systems containing fluorinated β -diketones and neutral donors were considered pertinent to this research. Systems consisting of mixtures of HTTA and neutral organophosphorus compounds have been extensively studied. Although many researchers have contributed to the elucidation of the nature of synergism in

this system, noteworthy contributions were made by Irving and Edgington (59-62), Sekine and Dyrssen (103-108) and Healy et al. (47-53). Several brief reviews have been published (31, 49,74,85). The reader is referred to the extensive review by Cary (22) for a comprehensive coverage of the major developments in synergic extraction of cations by mixtures of HTTA and neutral organophosphorus donors.

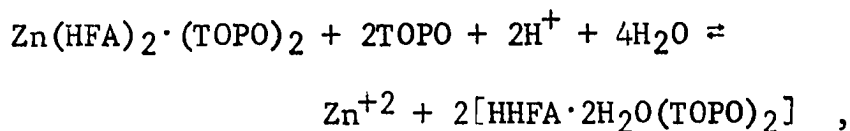
Investigations of the phenomenon of synergic enhancement in solvent extraction have demonstrated that synergism can occur in many instances for a large number of cations provided that certain conditions were fulfilled. For synergism to occur, it was necessary to have a cooperative action between at least two extractants. One is preferably a mono-acidic ligand which neutralizes the charge of the cation through chelation. The other extractant should displace any waters of hydration bonded to the neutral chelate and increase the hydrophobic character of the metal complex. The second extractant, which is usually a neutral donor, should be a weaker coordinating agent than the acidic ligand. In order to be synergically extracted the metal cation must not be coordinately saturated during the chelation reaction which produces the neutral complex.

Although synergic extraction systems containing HTTA and

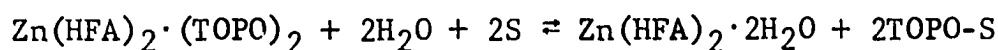
organophosphorus donors have been widely studied, few investigators have considered those fluorinated β -diketones which have been successfully used as gas chromatographic reagents. Li et al. (71) applied the method of continuous variation to the extraction of ^{65}Zn by hexane solutions of tri-n-octylphosphine oxide (TOPO) and the series of β -diketones, HAA, HTFA, HTTA, and HHFA. They interpreted their data as indicating the formation of the complexes $\text{Zn}(\text{HFA})_2(\text{TOPO})_2$ and $\text{Zn}(\text{TTA})_2 \cdot \text{TOPO}$. Other data were insufficient for making definite conclusions. The distribution ratios for Zn were found to increase in the order $\text{HAA} < \text{HTFA} < \text{HTTA} < \text{HHFA}$. These workers prepared solid $\text{Zn}(\text{HFA})_2 \cdot 2\text{H}_2\text{O}$ and the monohydrate, and isolated the oils, $\text{Zn}(\text{HFA})_2 \cdot (\text{TOPO})_2$ and $\text{Cu}(\text{HFA})_2 \cdot \text{TOPO}$. It was concluded from approximate solubility measurements on the hydrated and monoadduct TOPO complexes of U(VI) that the increased solubility of the mixed complex in the organic solvent could well be the basis of synergic extraction.

These same workers (127) later presented more conclusive evidence for the formation of the complexes, $\text{Zn}(\text{HFA})_2\text{TOPO}$ and $\text{Zn}(\text{HFA})_2(\text{TOPO})_2$ during extraction into hexane. Their extraction studies from 0.01 M HClO_4 indicated the formation of the monoadduct complex, while the diadduct species was extracted from acetate media at pH 5.0. On the basis of ultraviolet

and proton magnetic resonance studies the overall reaction,



was proposed to account for the destruction of synergism at $[\text{TOPO}] \geq 0.5 \text{ M}$. The addition of a large excess of the hydrogen bonding compounds, CHCl_3 and 2-ethylhexyl alcohol produced a destruction of synergism according to the overall reaction,



where S is the hydrogen-bonding compound.

Casey et al. (23) studied the synergic extraction of ^{64}Cu into the organic phase containing either TOPO or quinoline along with HAA, HTFA, HTTA or HHFA. For TOPO the distribution ratios increased in the order $\text{HAA} < \text{HTFA} < \text{HHFA} < \text{HTTA}$. The order for quinoline was found to be $\text{HAA} < \text{HHFA} < \text{HTFA} < \text{HTTA}$. These sequences are inconsistent and contradictory to the results which were previously discussed for the extraction of ^{65}Zn with these diketones.

Ke and Li (66) measured the equilibrium constants for the reaction of Cu(TFA)_2 chelates in benzene with n-butyl, n-hexyl, n-octyl and n-laurylamine (R_3N) and their corresponding hydrochlorides ($\text{R}_3\text{N} \cdot \text{HCl}$). Their spectrophotometric studies revealed several unexpected observations. The equilibrium constants for the reaction of Cu(TTA)_2 and Cu(TFA)_2

with the R_3N compounds were smaller than the corresponding constants for the reaction with organophosphates even though the amines are known to be more basic than the organophosphates. Steric hindrance of the amine groups was postulated as an explanation for this behavior. The equilibrium constants for adduct formation with $R_3N \cdot HCl$ were much greater than those of R_3N , in spite of the greater basicity of the latter. Bonding of the amine hydrochloride to the copper chelate through the chlorine atom was introduced as a mechanism for the minimization of steric effects and was proposed to account for the reversal in the expected behavior. Constants for the reaction of R_3N with $Cu(TTA)_2$ were observed to be larger than the reaction with $Cu(TFA)_2$ even though the latter is the stronger Lewis acid. Izatt et al. (65) reported the overall formation constants, $\log K_f = 17.2$ for $Cu(TFA)_2$ and $\log K_f = 19.2$ for $Cu(TTA)_2$. This behavior was attributed to the fact that the bulky R_3N group could force the 2-thenyl group out of the molecular plane thus destroying the resonance with the chelate ring. This out of plane bending was thought to prevent electron delocalization from the thenoyl group. It was postulated that this localization of the ring electron density increased the acidity of $Cu(TTA)_2$.

Fernando (38) discussed factors affecting adduct formation and made correlations between structure and properties of the adducts. Although studies on solid adduct complexes were primarily considered, much of the information presented is relevant to the understanding of the nature of synergism in liquid-liquid extraction. Several controversial issues have been resolved by spectral studies on copper chelates. It was established by infrared studies that in the diadducts of pyridine with $\text{Cu}(\text{TFA})_2$ both donor molecules had identical environments and were coordinated to the metal (42). Earlier workers (43) suggested that the second molecule of pyridine was not coordinated to bis(ethylacetoacetate)copper(II) but was free in the crystal lattice. The contention that the chelate ring was opened during the formation of the monoadduct of $\text{Cu}(\text{AA})_2$ with pyridine and that the vacant site was occupied by the donor molecule (125) was also disproved. The examination of the infrared spectra of quinoline and isoquinoline monoadducts of $\text{Cu}(\text{AA})_2$ showed no free carbonyl absorption in the $1600\text{-}1700\text{ cm}^{-1}$ region. This was taken as convincing evidence that acetylacetonate chelate rings were not ruptured as a result of adduct formation (56).

Fernando attributed the influence of the trifluoromethyl group on the stability of the adduct to the inductive effect

of fluorine. He pointed out that the logarithm of the first formation constant of copper chelates decreased when the methyl groups in acetylacetone are successively replaced by the electron-withdrawing $-CF_3$ group. This decrease in the stability of the metal chelate is indicated by the change in the logarithm of the formation constants from 9.2 to 6.6 to 2.7 for copper chelates of HAA, HTFA and HHFA respectively. This decrease in stability of the chelates produces a corresponding increase in the stability of the adduct, since the electron density around the metal cation is decreased by the electron withdrawing trifluoromethyl group. The weaker chelate, which is the stronger Lewis acid, thus has a greater tendency to participate in additional coordination to the neutral donor.

Pukanic and co-workers (88) studied hydrogen bonding between HTTA, HTFA and HHFA and the donors TBP, diethyl ethyl phosphonate (DEEP) and TOPO by proton and fluorine nuclear magnetic resonance. The equilibrium constants for hydrogen bond formation with the organophosphorus donors increased in the order $TBP < DEEP < TOPO$. The magnitude of the constants for the β -diketones increases in the order $HTTA \approx HTFA < HHFA$.

A search of the literature indicated one publication on the extraction of rare earths by the diketones and organophosphorus donors used in this research. Sekine and Ono (109) included trifluoroacetylacetone as one of the diketones in their study of the synergic extraction of Eu(III) from 0.1 M sodium perchlorate solution by TBP dissolved in chloroform. Their observations and conclusions from studies on HAA, benzoylacetone (HBA), HTFA, HBTA, and HTTA were:

1) The substitution of a methyl group in HAA or HTFA with benzoyl or thenoyl group increased the possibility of metal extraction, because this substitution increased the organophilic tendency of the metal chelate and reduced the formation of metal chelates in the aqueous phase. The substitution did not change the metal extraction equilibrium, $\text{Eu}^{+3} + 3\text{HA} \rightleftharpoons \text{MA}_3 + 3\text{H}^+$.

2) The β -diketones with one trifluoromethyl group extracted the metal ion from aqueous solutions at a lower pH than those without the $-\text{CF}_3$ group.

3) The substitution of one methyl group in acetylacetone or benzoylacetone with one trifluoromethyl group increased the ability of the respective metal chelates to form adducts with TBP in chloroform.

4) The formation of adducts of the chelates of HAA or

HTFA were not significantly altered by replacement of the methyl group with a benzoyl or thenoyl group.

While this thesis research was in progress, Honjyo (54) studied the effect of chelating ligands on the stability of the adducts of lutetium β -diketonates with TOPO in benzene. His series of ligands included the aliphatic compounds, HAA, dipropionylmethane (HDPM), pivaloylacetone (HPVA), diisobutyrylmethane (HDIBM), and dipivaloylmethane (HTHD); the aromatic ligands, HBA, naphthoylacetone (HNA) and dibenzoylmethane (HDBM); and the fluorinated β -diketones, HTFA, HHFA, HTTA and HBTA. The stability of the adducts increased and larger synergism appeared as aliphatic, aromatic and fluoromethyl groups were successively substituted for groups on the β -diketones. The stability of the adducts with TOPO increased in the order: aliphatic groups (HAA \approx HDPM < HPVA = HTHD = HDIBM) < aromatic groups (HBAA < HNA << HDBM) < trifluoromethyl groups (HTFA < HTTA < HBTA << HHFA). No significant steric effect of the terminal aliphatic or aromatic groups on the formation of adducts was observed. All of the β -diketones of Lu(III) formed monoadducts with TOPO, except for the mixed complex with HHFA which contained 2 molecules of the donor.

Although a considerable interest in the fundamental

aspects of synergism has been displayed, the potential of these systems for analytical separations and analysis has not been fully exploited. In most cases distribution ratios have been measured and compared with normal extraction systems. Separation factors for cations in synergic systems have been calculated by some investigators. Manning (73) investigated the extraction of rare earths, scandium and yttrium from nitric acid media into odorless kerosene solutions containing HTTA and dialkyl alkyl phosphonates. He concluded that steric effects were significant in the extraction of lanthanides in systems containing dibutyl butyl phosphonate or bis-(2-ethylhexyl) 2-ethylhexyl phosphonate and HTTA. He felt that this could lead to poor separation factors and suggested that synergic systems would seem to possess little practical application for improved separation of lanthanides, except in cases where the lower lanthanide chelates form disolvates and the higher lanthanides form monosolvates. Sekine and Dyrssen (102) studied the extraction of calcium and strontium by carbon tetrachloride solutions containing HTTA and donors, TOPO, TBP or methyl isobutyl ketone (MIBK). They proposed a selective separation of Ca and Sr from most other metals by extracting the latter at pH 4.0 with 0.1 M HTTA - 0.01 M TBP in CCl₄. By adjusting the pH to 6.6, 90% of the Ca and 30% of

the Sr, which remained in the aqueous phase, could be transferred to the organic phase. Most of the strontium could be back-extracted by washing the organic layer 3 times with water buffered at pH 6.6 with p-nitrophenol.

Healy (50) studied the extraction of alkali metals by benzene solutions of HTTA-TBP. The extraction of lithium was enhanced by a factor of up to 10^5 with a mixture of HTTA and TBP, compared to the extraction of either extractant alone. A remarkable improvement in separation factors of alkali metals was discovered. While the separation factors for alkali metals was never greater than 10 with HTTA alone, Healy found this factor to increase to >500 for Li/Na and $> 10^4$ for Li/K and Li/Cs in the presence of 0.1 M TBP in benzene. This behavior is opposite to that found for most other cations. Awwal (4) separated Ce(III) from fission products by a synergic extraction with 0.10 M HTTA + 0.25 M TBP in benzene. Aqueous nitrate phases at pH 2.8-3.1 were extracted to obtain this separation. A method for the spectrophotometric determination of manganese in steel has been based on the extraction of Mn(II) into a mixture of HTTA and pyridine (1). Taketatsu and Banks (121) developed an improved method for the spectrophotometric determination of Nd, Ho and Er in the presence of other metals. They utilized the synergic properties of

mixtures of HTTA and TOPO to quantitatively extract the rare earth metal into the organic phase. The enhanced absorption of the mixed chelates in the organic medium provided a more sensitive method of analysis than that obtained by employing previous methods which were based on absorption measurements of the rare earths in aqueous nitrate or perchlorate media. Lefort (70) separated plutonium from large amounts of uranium with a mixture of 0.1 M HTTA-0.02 M TBP in benzene. Less than 0.1% of the original uranium was extracted with the plutonium. Scribner and Kotecki (100) measured distribution curves for the extraction of the divalent transition elements Pd, Cu, Ni, Co, Zn and Cd. A mixture of 0.1 M HTFA-0.4 M isobutylamine in CHCl_3 was used for this synergic extraction. These investigators obtained extraction efficiencies of 99.9% in the pH range from 8 to 10. They reported that the organic phase was relatively unstable and could not be used after 2½ hours. Although it was stated that some of these adducts were gas chromatographed, no other record concerning these accomplishments was located in the literature.

Volatile Chelates of β -Diketones

One of the most striking properties of metal chelates of the β -diketones when compared to other chelate complexes is

the relative ease of volatilization at reasonably low temperatures and the greater thermal stability of β -ketoenolates.

Since the pioneering work of Berg and Truemper who measured the vapor pressures of acetylacetonates (12), the thermal behavior of β -diketone complexes has been extensively studied. Berg and Acosta (11) recently published a comprehensive study on the fractional sublimation of lanthanide, Sc, Th and uranyl chelates of HAA, HTFA, HHFA and HTHD. The hydrated rare earth chelates of HAA did not sublime while the anhydrous complexes of Sc(III), Th(IV), U(IV) and the uranyl cation were volatile and exhibited high thermal stabilities. This lack of volatility of the lanthanide acetylacetonates was explained on the basis that the hydrates were too polar to sublime. It was reasoned that the removal of the strongly bonded water in a vacuum led to thermal decomposition with the loss of water and acetylacetone. The dehydrated residue was reported to be a basic, non-volatile, polymerized, species. Thermal decomposition of the lanthanide trifluoroacetylacetonates was also extensive and this precluded separations by fractional sublimation. $\text{Th}(\text{TFA})_4$ was the only completely volatile and thermally stable chelate of this ligand. The rare earth hexafluoroacetylacetonates were reported to exhibit high thermal stability and volatility under vacuum conditions.

Berg indicated that mixtures of La-Dy, La-Er, La-Lu and La-Y could be successfully separated. However Bhaumik (14) studied the sublimation behavior of $\text{Eu}(\text{HFA})_3$ and reported that fluorescence analysis of the original and sublimed sample indicated partial decomposition. All of the dipivaloylmethane chelates were reported to be quantitatively sublimed and thermally stable. Sicre et al. (111) later published vapor pressures, heats of vaporization and heats of sublimation of the lanthanide dipivaloylmethane chelates.

Sievers and co-workers have been responsible for major developments in the area of the gas chromatography of the lanthanide elements. They attempted to chromatograph the hydrated neodymium trifluoroacetylacetonate chelate, but were unsuccessful (113). The presence of water had been previously postulated to cause the thermal instability of hydrated β -diketonates (24,25,86). Sievers and his colleagues felt that the nature of the ligand could greatly influence the hydrate formation and reasoned that a ligand in which steric crowding was significant could decrease the tendency for formation of hydrated complexes. They prepared the lanthanide chelates of 2,2,6,6-tetramethyl-3,5-heptanedione (HTHD) which were isolated as anhydrous complexes. These complexes were success-

fully chromatographed and marked the first achievement in the chromatography of rare earth elements (34).

After it was demonstrated that fluorine containing β -diketones formed more volatile chelates than the corresponding hydrocarbon derivatives, Springer et al. (116) synthesized 1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl-4,6-octanedione (HFOD). This ligand retained the desired steric effect of the bulky HTHD diketone and possessed the added advantage of volatility, which was induced by the fluorine constituent. The chelates of HFOD which were isolated as monohydrates, could be easily dehydrated without apparent hydrolysis under vacuum conditions. The anhydrous chelates were successfully gas chromatographed and were found to be more volatile than the chelates of HTHD. These accomplishments by Sievers and co-workers are significant achievements, however, the techniques used by these workers are not suitable for practical analytical applications. Their method required the preparation, dehydration, and dissolution of solid chelates in a suitable solvent before the chelates could be chromatographed.

Butts and Banks (20) recognized the inadequacies in the technique used by Sievers and co-workers. These investigators felt that a solvent extraction technique was the most convenient method for the preparation of chromatographable chelates.

They prepared anhydrous mixed chelates of the rare earths by the synergic extraction of the rare earths with a solution of HHFA and TBP in cyclohexane. The organic phase containing the extracted species was sampled and directly injected into the gas chromatograph. The first successful gas chromatography of mixed lanthanide chelates demonstrated the soundness of their approach to the problem of developing practical analytical methods for analysis of cations by gas chromatography.

Thermogravimetric analysis has been conveniently used as a tool for determining the relative volatilities and thermal stabilities of chelates. Eisentraut and Sievers (35) determined the relative volatilities of some transition metal chelates of HTHD, HHFA, HFHD, HFOD, HTFA and HAA. Chelates of the trivalent elements, Fe, Rh, Al and Cr were studied. The lanthanide-HTHD complexes were thermogravimetrically analyzed. Sievers et al. (112) reported thermograms for the hydrated HTFA and HTTA chelates of europium, $(\text{CH}_3)_4\text{N}[\text{Eu}(\text{HFA})_4]$ and $(\text{C}_2\text{H}_5)_3\text{NH}[\text{Eu}(\text{HFA})_4]$. Tanaka et al. (123) reported thermogravimetric and gas chromatography studies on eleven rare earth chelates of 1,1,1-trifluoro-5,5-dimethylhexane-2,4-dione.

Lippard (72) discovered that an eight coordinated β -diketonate of yttrium and cesium could be easily sublimed in air

and in vacuo without apparent decomposition. They found that the compound, CsY(HFA)_4 , sublimed at temperatures ranging from 180 to 230°C. This demonstration of the stability of an ion association complex in the gas phase stimulated investigations by other workers. Belcher et al. (6) prepared chelates of composition, L(R.E.)A_4 , where L is a series of alkali metals. HTFA, HHFA and trifluoroacetylaloylmethane chelates were prepared and studied by mass spectral analysis, infrared and ultraviolet methods. Ismail and co-workers (64) also studied the chelates, L(R.E.)A_4 , of the ligand 1,1,1-trifluoro-5,5-dimethyl-2,4-hexanedione. They applied Raman, NMR and fluorescence spectroscopy in their studies of these compounds.

Volatile fluorinated β -diketone chelates of other metals have been reported. Belcher et al. (7) studied the sodium chelates of $\text{CF}_3\text{COCH}_2\text{COR}$ where R is the methyl, neopentyl, trifluoromethyl and C_6F_{11} group. In view of the partial sublimation of alkali chelates of HTHD, they synthesized the bulky ligand, 1-(undecafluorobicyclo[2.2.1.]heptan-1-yl)-4,4,4-trifluorobutan-2,4-dione. Although the sodium chelate of this ligand sublimed at 250°C without apparent decomposition, it was still less volatile than the HHFA chelate. Schweitzer et al. (97) prepared 14 aliphatic fluorocarbon and seven

hydrocarbon β -diketone chelates of Pb(II). Vapor pressures were measured and thermal stabilities of the chelates at 100°C were determined.

Procedures for the preparation of HTFA and HHFA chelates have been described by several investigators. Anderson and Brenner (3) prepared $\text{Re}(\text{HFA})_3$. $\text{Ti}(\text{HFA})_3$ was prepared by Fry and Watt (41). Fay and Piper (36) synthesized HTFA chelates of the trivalent metals Cr, Co, Rh, Al, Ga, In, Mn and Fe. Larsen et al. (69) prepared the Zr(IV) and Hf(IV) HTFA chelates and measured densities of the solid complexes. Chatteraj et al. (26) characterized and studied the hexafluoroacetylacetonone chelates of Zr(IV) and Hf(IV). Infrared, NMR, DTA, TGA, mass spectral and chemical analysis data were reported. Additional data on the physical properties of trifluoroacetylacetonone and hexafluoroacetylacetonone chelates were compiled in the recent monograph by Moshier and Sievers (81).

EXPERIMENTAL AND ANALYTICAL PROCEDURES

Apparatus

Gamma ray activities from radioisotopes were monitored with a single channel, well-type scintillation counter manufactured by Radiation Instruments Development Laboratory. The gamma ray counter was equipped with a thallium-doped sodium iodide detector. A Cary Model 16 recording spectrophotometer, a Cary 14 and a Beckman DU spectrophotometer were used in spectrophotometric measurements. Beckman pH standards and a Beckman Model G pH meter with a saturated calomel reference electrode and a glass indicator electrode were employed in pH measurements. Atomic absorption analyses were made with a Perkin Elmer 303 Spectrophotometer. The DuPont 900 Differential Thermal Analyzer and 950 Thermogravimetric Analyzer were used to record thermograms. The Beckman Model GC 4 was used for gas chromatography of reagents and chelates.

Reagents

Solvents

Reagent-grade thiophene-free benzene and cyclohexane were used as diluents in solvent extraction studies. Spectroquality solvents were employed for spectrophotometric analysis of the organic phases.

Spectrophotometric reagents and indicator solutions

Xylenol orange [3,3'-bis(N,N'-di-(carboxymethyl)-amino-methyl)-o-cresol sulfonphthalein], obtained from LaMont Laboratories, was used as a 0.5% aqueous solution.

Arsenazo I [3-(2-arsonophenylazo)-4,5-dihydroxy-2,7-naphthalenedisulfonic acid trisodium salt] was obtained from Eastman Chemical Company and was used as a 1.00×10^{-3} M aqueous solution. Arsenazo III (1,8-dihydroxynaphthalene-3,6-disulfonic acid-2,7-bis[(azo-2)-phenylarsonic acid]) obtained from Aldrich Chemical Company was used as a 0.1% aqueous solution. Thorin [1-(2-arsonophenylazo)-2-naphthol-3,6-disulfonic acid] was used as a 0.1% aqueous solution.

Buffers

Aqueous acetate buffers were prepared by mixing 0.20 M solutions of sodium acetate and 0.20 M acetic acid according to tables in Vogel's text (126). A series of stock buffer solutions were prepared by mixing different molar ratios of 1.0 M sodium acetate and 1.0 M HCl. Appropriate amounts of NaCl were added to maintain a total equilibrium ionic strength of 1.0. Solutions of 1.0 M NH_4OH and 1.0 M NH_4Cl were employed for pH control at basic conditions.

Standard cation solutions

Standard solutions of Zn(II), Cu(II) and Fe(III) were

made by dissolving appropriate quantities of Bunker Hill electrolytic zinc (99.99%), Fisher Certified iron (99.9%) and copper (99.999%) in minimal volumes of HCl or HNO₃. After dissolution the samples were evaporated to dryness and diluted to volume with deionized water. At least three successive evaporations with concentrated HCl were made when HNO₃ was employed for dissolution. Iron(III) solutions were diluted to volume with 0.10 M HNO₃ to prevent precipitation and used immediately. A standard aluminum stock solution was prepared by dissolving the high purity wire in a small volume of HCl containing a drop of mercury as a catalyst. After separation from the mercury the sample was diluted to volume with deionized water. A uranium(VI) solution was prepared by dissolving pure U₃O₈ in a small amount of HNO₃. After repeated evaporations with HCl the sample was diluted to volume. The prepared solution was standardized by passing aliquots through a lead reductor into a solution of Fe(III). The Fe(II) produced was titrated with a standard solution of Ce(IV) using ferroin as the indicator. Standard calcium solutions were prepared by dissolving primary standard CaCO₃, a G. F. Smith Reagent, in a minimal volume of 0.10 M HCl and diluting to volume with deionized H₂O. Th(IV) and Sc(III) solutions in aqueous chloride media were standardized by direct EDTA titration

at pH 2 and 3 to 4 respectively. Xylenol orange was used as the indicator (67,68). Standard solutions of the rare earths were prepared by dissolving the 99.9% pure oxides in HCl and diluting to volume. The prepared solutions were titrated directly with EDTA using xylenol orange as the indicator.

Uranyl solutions 1.0 M in HCl were passed through a lead reductor according to procedures in the Ames Laboratory Manual. The eluate was collected in a suction flask which was stoppered with a two-hole rubber stopper through which a nitrogen inlet and the tip of the column were placed. The flask was purged continuously with nitrogen throughout the reduction. The U(IV) solution was diluted to volume with 1.0029 M HCl and transferred to an automatic adjustable buret. The uranium solution was stored under a nitrogen atmosphere in the closed buret system which was protected from light by opaque tape. A positive nitrogen flow was always maintained whenever the U(IV) solution was dispensed from the buret. Aliquots of the stock solution were periodically titrated as previously described for the standardization of uranyl solutions. The following changes in the molarity of the stock solution were recorded: 4 hours, 0.07640 M; 4 days, 0.07673 M; 6 days, 0.07646 M; and 22 days, 0.07603 M. Rydberg (93)

found U(IV) solutions to change a few percent per month. Aliquots of the stock solution were titrated immediately before use in experiments.

Radioisotopes

^{147}Nd , ^{170}Tm and ^{46}Sc were prepared by neutron irradiation of the pure oxides at the Ames Lab Research Reactor. The irradiated samples were dissolved in concentrated HCl. The excess acid was removed by evaporation and the tracers were diluted to volume with deionized H_2O . The final pH of the stock tracer solutions was adjusted to 2.0-3.5 with dilute HCl. $^{152,154}\text{Eu}$ was purchased from the isotopes division of Oak Ridge National Laboratory. ^{65}Zn in 1.0 M HCl and ^{59}Fe in 4.0 M HCl were obtained from New England Nuclear Corporation.

β -Diketones and organophosphorus compounds

HTFA, HHFA and HFOD were obtained from Peninsula Chem-research, Incorporated. Gas chromatograms of the freshly distilled reagents showed no detectable impurities. HFHD and HDODEFOD were obtained from the Ames Laboratory.² TBP, obtained from Fisher Scientific Company, was purified by procedures of Irving and Edgington (58). Gas chromatograms

²Prepared by John J. Richard, assistant chemist, Ames Laboratory.

confirmed the purity of the distilled reagent. TFEP and PFPP were prepared by John J. Richard. These compounds were distilled before use and gas chromatograms indicated highly pure products. The purity of the extractants were periodically monitored by gas chromatography. Repeated purification of TBP, distillation of β -diketones and gas chromatography of stock quantities of these compounds were maintained throughout the extraction study. All other reagents were analytical grade.

Measurement of Distribution Ratios

Organic phases were prepared by pipeting the appropriate amounts of the pure liquid extractants, equilibrated in a constant temperature bath maintained at 25°C, into volumetric flasks containing the organic solvent. The sample was diluted to volume with the organic diluent which was presaturated with deionized water or an aqueous phase of ionic strength 0.10. This procedure proved to be superior to methods employing direct weighing techniques for preparation of solutions of the volatile fluorinated β -diketones. The procedure adopted allowed easy duplication of reagent concentrations in subsequently prepared solutions and decreased the potential hazard of exposure to fumes of the volatile β -diketones. The

accuracy of this procedure for preparation of organic phases containing known quantities of β -diketones was confirmed by titration of aliquots of the solution in tertiary butyl alcohol with tetrabutylammonium hydroxide in benzene. Thymol blue or 2,4-dinitroaniline were used as indicators. Organic phases were always freshly prepared before use in extraction studies. This precaution prevented changes in the initial extractant concentration that could occur upon storage of a stock organic solution of the extractants.

Aqueous phases were prepared by mixing appropriate amounts of tracer and/or carrier, and aliquots of a buffer solution of ionic strength 1.0 M. The mixture was diluted ten-fold with deionized water which was presaturated with the organic solvent, to produce an aqueous phase of ionic strength 0.10.

In those studies involving applications of the law of mass action, equal volumes of aqueous and organic phases were placed in 15-ml, glass-stoppered centrifuge tubes. The tubes were taped, wrapped in aluminum foil and equilibrated by agitation on a Burrel wrist-action shaker until equilibrium was achieved. Equilibration times ranging from 30 minutes to 13 hours were allowed when necessary to ensure equilibrium. No

volume changes were observed to occur during equilibration. After equilibrium was achieved the tubes and their contents were centrifuged and aliquots of each phase were removed for measurement of the radioactivity. To prevent cross contamination of the lower phase, a positive air pressure was maintained in the pipet as it was passed through the upper phase. After corrections for background activity the distribution ratio was calculated by dividing the activity of the organic phase by that of the aqueous. Similar procedures were employed for those experiments in which tracers were not utilized. In these cases distribution ratios were calculated after spectrophotometric analysis of the aqueous and/or organic phase. Cyclohexane was the solvent utilized in all synergic extractions.

Mole Ratio Studies

Several experiments were performed to study the distribution of various cations as a function of molar ratios of TBP and β -diketone in the organic phase. A series of organic phases in which the concentration of β -diketone was held constant and the molar ratio of TBP to metal in the aqueous phase was varied, were prepared. Similarly, phases containing the same amount of TBP and different molar ratios of

β -diketone to cation were prepared. Aqueous phases containing approximately 0.01 M cation were prepared by diluting 0.10 M solutions with a pH 5.46 acetic acid-sodium acetate buffer. The initial cation concentrations of rare earths were determined by direct EDTA titration using xylenol orange as the indicator. Equal volumes of aqueous and organic phases were equilibrated as previously described.

The percentage extraction of cations was calculated from measurements of the gamma ray activity in the aqueous and organic phases. In similar experiments the extraction of the chelate complexes of Pr, Nd, Ho and Er was followed by recording the absorption spectra on the Cary 16 spectrophotometer.

Determination of Acid Dissociation Constants of β -Diketones

The apparent acid dissociation constants of HAA, HTFA, HHFA, HFOD and HFHD were determined by potentiometric titration of aqueous solutions of the β -diketones at an ionic strength of 0.1. Aliquots of the β -diketones and appropriate amounts of 1.0 M NaCl solution were diluted to volume with deionized water. The solutions were shaken until complete dissolution occurred or until saturated aqueous phases were obtained. Aliquots of the prepared solutions were pipeted into a teflon beaker containing a magnetic stirring bar. The

beaker was fitted with a rubber stopper containing holes through which the electrodes and buret tip were placed. The pKa values were estimated from the data obtained from potentiometric titrations of the β -diketones with a standard solution of sodium hydroxide. The measured values for HAA, HTFA, and HHFA agreed quite well with those reported in the literature (118).

Determination of Cations

Aluminum: A Perkin Elmer Atomic Absorption Spectrophotometer and an aluminum hollow cathode lamp were employed for the estimation of aluminum in aqueous phases.

Calcium: The method of Ferguson et al. was used for the spectrophotometric estimation of Ca(II) with chlorophosphonazo (III) (37).

Copper: A spectrophotometric method described by Irving and Al-Niami (57) was used for the determination of copper(II).

Rare Earths and Yttrium: The procedure of Fritz et al. (40) was used for the spectrophotometric determination of La, Pr, Lu and Y with Arsenazo.

Thorium: Thorin was used for the spectrophotometric determination of thorium. Procedures described by Thompson, Perry and Byerly were employed (124). The more sensitive method of

Savvin (94) which utilizes Arsenazo III was used for thorium concentrations in the range 10^{-6} to 10^{-7} molar.

Uranium: The procedure of Fritz and Richard (39) was employed for the spectrophotometric determination of the uranyl ion.

Preparation of Metal Chelates

The method of Haszeldine (46) was modified for the preparation of the U(IV)-HTFA chelate. The green colored aqueous solution containing U(IV) was adjusted to pH 2.0 to 3.0 by the dropwise addition of a dilute solution of NaOH. The gelatinous, khaki green colored precipitate obtained by the addition of excess trifluoroacetylacetone was dissolved by and extracted into benzene. The benzene phase was transferred to a container which allowed nitrogen to be bubbled through the solution. A nitrogen-filled polyethylene glove bag permitted all previous operations to be conducted in an inert atmosphere. The capped bubbler was removed from the glove bag and the solvent was evaporated by bubbling nitrogen through the solution which was heated by means of a water bath. The dissolution and evaporation procedures were repeated.

The U(IV)-HHFA chelate was prepared by repeated extraction of an aqueous solution of the cation with excess HHFA in

ether. The solid chelate was obtained by the previously described evaporation technique. The solid chelates were stored in opaque vials under a nitrogen atmosphere. Analysis of the complexes showed 27.81 and 22.60 percent uranium for the HTFA and HHFA chelates, respectively. The calculated values were 28.00 and 22.32 percent, respectively.

The hydrated R.E.-HTFA and R.E.-HHFA chelates of Nd, Eu and Tm were prepared by standard procedures (7,45) and respectively recrystallized from benzene and n-hexane. Thermogravimetric analysis showed the stoichiometry of hydration to be 3.3, 3.2 and 3.3 respectively for the R.E.-HHFA chelates of Nd, Eu and Tm. The corresponding data for the R.E.-HTFA chelates were 2.6, 2.6 and 3.0. The data for the chelates of HHFA indicated that adsorbed moisture was not completely removed by drying in air. No attempts to dry the chelates in a vacuum or desiccator were made since β -diketone chelates of the rare earths may hydrolyze (86).

$\text{Eu}(\text{TFA})_3 \cdot 3\text{H}_2\text{O}$ was purchased from Eastman Organic Chemicals, Inc. The infrared spectra of the prepared chelates showed the characteristic absorption frequencies observed in the spectrum of the purchased compound. The spectra of the R.E.-HHFA chelates agreed well with data reported by Morris (79). The experimental and theoretical metal contents for

the Tm(III) chelate of HTFA were 24.79% and 24.77% respectively. The corresponding data for the Tm(III) chelate of HHFA were 20.59% and 20.01%.

The adduct complexes of rare earths were prepared by solvent extraction techniques. Aqueous phases containing the rare earth cations were buffered at pH 5.27 with a sodium acetate-acetic acid solution and equilibrated in separatory funnels with equal volumes of cyclohexane containing a 3:1 ratio of the β -diketone and a 2:1 ratio of TBP to rare earth. The organic solvent was evaporated by the gentle air flow in a closed hood. It was not possible to recrystallize the mixed chelates which were isolated as oils. No precipitation of the mixed chelates occurred upon dissolution in ether and cooling in a dry ice-acetone mixture. Infrared data on the HHFA-TBP chelates were recently reported by Butts (19).

Spectrophotometric Determination of U(IV) in Organic Solvents

A procedure was developed for the spectrophotometric determination of U(IV). Known quantities of the solid U(IV) chelates were dissolved in benzene, cyclohexane containing 0.0704 M HHFA + 0.073 M TBP or cyclohexane containing 0.082 M HTFA + 0.073 M TBP. Absorbance versus time data are shown in Table 1.

Table 1. Absorbance versus time data for uranium(IV) chelates

Time	$\lambda = 611 \text{ nm}$	$\lambda = 657.5 \text{ nm}$		$\lambda = 651 \text{ nm}$	$\lambda = 647.5 \text{ nm}$
	U(HFA) ₄ ·2TBP Dissolved solid	U(TFA) ₄ ·2TBP Dissolved solid	Extracted	Dissolved solid	U(IV) (1.0 M HCl)
15 min.	0.436	0.337	0.397	0.2528	0.433
30	0.432		0.398	0.2524	
50		0.334	0.397	0.2518	
60				0.2505	
90	0.430		0.397		
110	0.428	0.332	0.397		
135		0.333	0.396		
3 hrs.	0.428		0.396		
10					0.432
14			0.396		
26					0.417
6 days	0.427				

The molar absorptivities of the compounds $U(HFA)_4 \cdot 2TBP$, $U(TFA)_4 \cdot 2TBP$, $U(TFA)_4$ and $U(IV)$ in 1.0 M HCl for the wavelengths given in Table 1 were 85.6, 67.0, 50.6 and 57.6 liters $cm^{-1}mole^{-1}$. Linear Beer's law plots were obtained for concentrations up to 5×10^{-3} M for the $U(IV)$ -HHFA-TBP and the $U(IV)$ -HTFA-TBP complexes.

These data show that extraction studies by direct spectrophotometric measurement of the $U(IV)$ species in the organic phase can be accomplished if precautions are taken to minimize oxidation during the experiments. All containers were purged with nitrogen before use, and covered immediately after purging and addition of $U(IV)$ solutions. Aliquots of the $U(IV)$ solutions were delivered from a closed, nitrogen-purged, automatic filling buret or were pipeted with syringes.

Extraction studies were made by equilibrating equal volumes of aqueous and organic phase for forty-five minutes with a wrist-action shaker placed in a nitrogen filled drybox. The total uranium remaining in the aqueous phase at equilibrium was determined by oxidation with nitric acid followed by a spectrophotometric measurement of the $U(VI)$ -arsenazo complex. All distribution data for the $U(IV)$ cation were expressed as $K_D = [U^{+4}]_o/[UO_2^{+2}]$.

THEORETICAL ASPECTS OF LIQUID-LIQUID EXTRACTION

The solvent extraction process usually involves the distribution of solute species, initially present in an aqueous phase, into an immiscible organic solvent. In the ideal situation such a system is composed of three components, two completely immiscible liquid phases which are infinitely dilute in a solute that distributes between the two solvents as a monomer. When both phases are in equilibrium with respect to changes in concentration of the distributing specie, the chemical potentials of the solute in both phases are equivalent,

$$\mu_{(o)} = \mu. \quad (1)$$

By substitution into this equation one obtains the following expression,

$$\mu_{s,(o)}^{\circ} + RT \ln C_{s,(o)} + RT \ln \gamma_{s,(o)} = \mu_s^{\circ} + RT \ln C_s + RT \ln \gamma_s, \quad (2)$$

in which $\mu_{s,(o)}^{\circ}$ and μ_s° represent the standard state chemical potentials of the solute; $C_{s,(o)}$ and C_s denote the solute concentration and $\gamma_{s,(o)}$ and γ_s are the activity coefficients of the solute in the organic and aqueous phases, respectively.

Equation 2 may be rearranged to give

$$\frac{C_{s,(o)}}{C_s} = \frac{\gamma_s}{\gamma_{s,(o)}} \left[e^{-(\mu_{s,(o)}^0 - \mu_s^0)/RT} \right] \quad (3)$$

In the case of low concentrations of solute, $\gamma_{s,(o)}$ and γ_s approach unity and the Nernst distribution law mathematically relates the partitioning of the solute to the ratio of its concentration in the two phases. Thus, Eq. 3 has a constant value and reduces to

$$P = \frac{C_{s,(o)}}{C_s} . \quad (4)$$

This expression for P, the partition or distribution coefficient, is valid when the solute has the same composition in both phases.

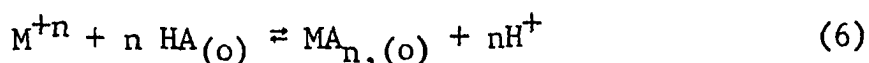
Practical analytical solvent extraction systems are usually composed of numerous constituents which simultaneously undergo various chemical reactions in both phases to produce species that distribute according to the overall equilibrium process. When the distributing species assume different chemical forms in the mutually saturated immiscible phases the equation,

$$K_D = \frac{[C]}{[C]} , \quad (5)$$

is appropriate. K_D is the distribution ratio and is defined as the ratio of the total concentration of the distributing species in the organic phase to that in the aqueous phase.

If only neutral, uncharged species are extracted when a metal

ion of charge n (M^{+n}) distributes between an aqueous and organic phase containing only the chelating ligand (HA)³ the reaction may be represented by a general expression. In the absence of the formation of polynuclear, metal-containing species in the organic phase the principal reaction,



occurs, where A represents the corresponding anion of the chelating ligand and subscript (o) denotes species in the organic phase. Unsubscripted quantities refer to those in the aqueous phase.

Although the overall reaction is given by Eq. 6, the equilibrium process depends upon several reactions occurring in both phases. The β -diketone (HA) partitions, enolizes and dissociates. The partitioning reaction, represented by $HA_{(o)} \rightleftharpoons HA$, is controlled by the partition coefficient $P_{HA} = [HA]_o/[HA]$. The enolization reaction, Keto \rightleftharpoons Enol, and the dissociation reaction, $HA \rightleftharpoons H^+ + A^-$, regulated by the acid dissociation constant, $K_a = [H^+][A^-]/[HA]$, also occur simultaneously. Other ions including chloride, acetate, hydroxide and sodium are present in the aqueous phase. At low $[OH^-]$ and for negligible complexation by Cl^- and Ac^- , the principal

³HA may be any one of the previously named β -diketones.

reaction of M^{+n} in the aqueous phase yields complexes of the form, MA^{n-1} , MA_2^{n-2} , ..., and MA_n . The relative concentrations of the β -diketonate complexes in the aqueous phase are governed by the cumulative stability constants,

$$\beta_1 = \frac{[MA]}{[M][A]}, \quad \beta_2 = \frac{[MA_2]}{[M][A]^2} \quad \text{and} \quad \beta_n = \frac{[MA_n]}{[M][A]^n}.$$

Upon neutralization of the charge on the cation the hydrophobic complex, MA_n , distributed between the two phases according to its partition coefficient,

$$P_{MA_n} = \frac{[MA_n]_o}{[MA_n]}.$$

If during the equilibrium process variations in activity coefficients of reactants in the organic phase are minimized by employing dilute solutions of the extractants in inert diluents and the activity coefficients in the aqueous phase are controlled by maintaining a constant ionic strength, the concentration equilibrium constant for reaction 6 can be written as

$$K_{eq}^o = \frac{[MA_n]_o [H]^n}{[M][HA]_o^n} \quad (7)$$

where $[M]$ is the total concentration of metal in the aqueous phase. The superscript o indicates an equilibrium constant for an extraction in the absence of a synergist and $[]$ repre-

sents molar concentration except for $[H]$ which is the activity measured by a pH meter. Ionic charges have been omitted for simplicity. Substitution of the distribution ratio, $K_D^0 = [MA_n]_o / [M]$, into Equation 7 produces

$$K_{eq}^0 = \frac{K_D [H]^n}{[HA]_o^n} \quad (8)$$

The dependence of the equilibrium constant on all factors contributing to the distribution ratio is given by

$$K_{eq}^0 = \frac{P_{MA_n} \beta_n K_a^n}{P_{HA}^n (1 + \sum_{n=1}^n \beta_n [A]^n)} \quad (9)$$

Equation 8 is transformed into the corresponding log expression,

$$\log K_D^0 = \log K_{eq}^0 + n \log [HA]_o - n \log [H]. \quad (10)$$

Equation 10 is important in fundamental extraction studies since it provides a means of determining the numbers of molecules of reactants or products participating in the extraction process. From this expression the value of the coefficients in reaction 6 may be determined by experimental measurement of K_D^0 as a function of the concentration of one

⁴See APPENDIX for derivations.

variable while maintaining the concentrations of the other species at constant values. At constant pH, Eq. 10 is reduced to

$$\log K_D^0 = \log K' + n \log[HA]_0 \quad (11)$$

where K' is a constant. Graphical plots of $\log K_D^0$ versus $\log[HA]_0$ gives a linear plot with slope n and intercept $\log K'$. The numerical value of the equilibrium constant for the chelation reaction is obtained at $[HA]_0 = 0$ where

$$\log K_{eq}^0 = \log K_D^0 - n \text{ pH}. \quad (12)$$

An average value of the equilibrium constant can also be calculated from data in the linear region of the graphical plot. Similarly, the number of hydrogen ions involved in the reaction can be obtained and the composition of the extracted chelate deduced.

Equation 10 can be transformed into an analytically useful expression for choosing conditions for the liquid-liquid separation of cations. The percentage of extraction,⁵ E , is defined as the ratio of the concentration of the distributing species in the organic phase to the total concentration in both phases. If both phases are of equal volume (E) is related to the distribution ratio by the expression,

⁵ See APPENDIX for E relationships.

$$E = \frac{K_D(100)}{K_D+1} \quad (13)$$

Equation 13 may be rearranged to

$$K_D = \frac{E}{100-E} \quad \text{or} \quad \log K_D = \log \left(\frac{E}{100-E} \right) \quad (14)$$

Substitution into Eq. 10 now produces the equation,

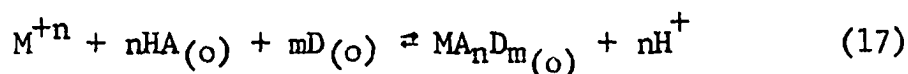
$$\log E - \log(100-E) = \log K_{eq}^0 + n \log[HA]_0 + n \text{ pH} \quad (15)$$

At 50% extraction the pH is designated as $\text{pH}_{\frac{1}{2}}$. Equation 15 reduces to

$$\text{pH}_{\frac{1}{2}}^0 = -\frac{1}{n} \log K_{eq}^0 - \log[HA]_0 \quad (16)$$

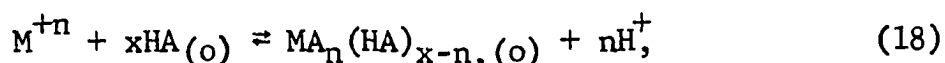
Distribution curves for analytical purposes are generally presented as plots of E (ordinate) versus pH (abscissa). These plots for different metals at constant $[HA]_0$ form a family of sigmoid curves which are positioned along the pH axis depending on the magnitude of K_{eq}^0 . The difference in $\text{pH}_{\frac{1}{2}}$ values and the quotient of the distribution ratios, are related to separability. The separation factor is defined as follows: $\text{S.F.} = K_{D1}^0 / K_{D2}^0$.

In synergic extraction systems containing HA and a neutral donor (D),⁶ the following principal reaction



⁶Donor compounds used in this study include TBP, TFEP and PFPP.

occurs. Other reactions are possible in the organic phase. The enol form of the chelating ligand can interact with the donor through hydrogen bonding, $x\text{HA}_{(o)} + y\text{D}_{(o)} \rightleftharpoons (\text{HA})_x\text{D}_y_{(o)}$. The donor can extract water and acid into the organic phase by the reactions, $\text{D}_{(o)} + x\text{H}_2\text{O} \rightleftharpoons \text{D}(\text{H}_2\text{O})_{x,(o)}$ and $\text{D}_{(o)} + x\text{HX} \rightleftharpoons \text{D}(\text{HX})_{x,(o)}$. Contributions from these reactions are seldom important, but when significant the effects of these side reactions are evident by a decrease in the synergic effect. At sufficiently high $[\text{HA}]_o$ a neutral molecule of the β -diketone can assume the role of a donor. The occurrence of this reaction,



may be detected by the mass action effect.

The equilibrium constant corresponding to reaction 17 may be written as

$$K_{\text{eq}} = \frac{[\text{MA}_n\text{D}_m]_o [\text{H}]^n}{[\text{M}][\text{HA}]_o^n [\text{D}]_o^m} \quad (19)$$

It follows that substitution of the distribution ratio, K_D , into Eq. 19 produces

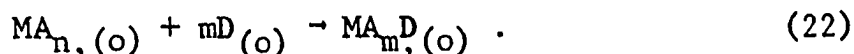
$$K_{\text{eq}} = \frac{K_D [\text{H}]^n}{[\text{HA}]_o^n [\text{D}]_o^m} \quad (20)$$

The corresponding logarithmic expression

$$\log K_{eq} = \log K_D - n \log [HA]_o - m \log [D]_o + n \log [H]^{7,8} \quad (21)$$

may be used to deduce the composition of the extracted adduct complex.

The adduct reaction in the organic phase between the metal chelate and donor is given by



The overall formation constant for this reaction is represented by

$$\beta_m = \frac{K_{eq}}{K_{eq}^o} = \frac{\text{Eq. 19}}{\text{Eq. 9}} = \frac{[MA_{m,D}]_o}{[MA]_{n,o} [D]_o^m} \quad (23)$$

The equation for the synergic system which corresponds to Eq. 7 can be written as⁹

$$K_{eq} = \frac{P_{MA_n} \beta_n K_a^n (1 + \sum_{m=1}^m \beta_m [D]_o^m)}{P_{HA}^n [D]_o^m (1 + \sum_{n=1}^n \beta_n [A]_o^n)} \quad (24)$$

The chemical equilibria and mathematical relationships presented in this discussion provided the basis for planning

⁷See APPENDIX for derivation.

⁸The previous discussion for expression 10 also applies here.

⁹See APPENDIX for derivation.

experiments and interpreting the results obtained from the fundamental extraction studies conducted during this research.

RESULTS AND DISCUSSION

Liquid-Liquid Extraction with Hexafluoroacetylacetone

The poor efficiency of the extraction of most metals by HHFA is well documented in the literature.¹⁰ The data in Table 2 show this same behavior for the extraction of thulium into cyclohexane. The distribution of thulium into solutions of HHFA in benzene is seen to be appreciable for tracer quantities (2.6×10^{-6} M) of this rare earth. The utility of HHFA as an extractant is quite limited since the extraction of lanthanides with β -diketones is expected to diminish with a decrease in atomic number (17) and the poor extraction of most cations by this ligand would severely limit the possibilities for useful separations by liquid-liquid extraction.

Table 2. Extraction of ^{170}Tm by 0.070 M solutions of HHFA in cyclohexane or benzene

Cyclohexane			Benzene		
pH	K_D°	E	pH	K_D°	E
3.38	0.404	28.8	2.78	0.019	1.84
4.38	0.751	42.9	3.68	0.822	45.1
4.42	0.914	47.7	3.85	1.37	57.8
8.26	0.459	31.5	4.70	11.2	91.8
9.00	0.013	1.3	8.34	2.15	68.3
			9.00	0.01	1.26

¹⁰See LITERATURE REVIEW.

The rate of extraction of thulium from an aqueous acetate-chloride solution at pH 1.38 into cyclohexane 0.05 M in HHFA + 0.05 M in TBP was briefly studied to determine the appropriate equilibration periods which were necessary for the establishment of equilibrium. The data in Table 3 show a very rapid extraction in this system. Although no significant variation in K_D occurred after equilibration for fifteen minutes, phases containing lower reagent concentrations were equilibrated at least 3-4 hours in order to ensure that equilibrium was attained.

Table 3. Distribution of Tm(III) versus time in the HHFA-TBP cyclohexane system

Time	K_D	Time	K_D
10 min.	63.7	1 hr.	23.2
15 min.	23.7	2 hr.	22.6
30 min.	21.2	3 hr.	27.8
45 min.	25.5		

[HHFA] = 0.05 M
 [TBP] = 0.05 M
 pH = 1.38
 [Tm⁺³] = 1.728 x 10⁻³ M

The effect of cation concentration on the distribution of neodymium and thulium is reported in Table 4. A constant distribution ratio was obtained at $[M] \leq 10^{-5}$ M.

Table 4. Cation concentration effects on distribution of lanthanides between aqueous acetate-chloride media and cyclohexane containing HHFA and TBP

[HHFA] = 0.070 <u>M</u> [TBP] = 0.011 <u>M</u> pH = 1.95		[HHFA] = 0.014 <u>M</u> [TBP] = .011 <u>M</u> pH = 1.87	
[Nd ⁺³]	K _D	[Tm ⁺³]	K _D
3.18 x 10 ⁻⁴	24.3	3.55 x 10 ⁻⁴	26.4
1.48 x 10 ⁻⁵	31.2	2.60 x 10 ⁻⁵	41.0
5.92 x 10 ⁻⁶	34.0	1.04 x 10 ⁻⁵	56.3
2.96 x 10 ⁻⁶	34.0	2.60 x 10 ⁻⁶	50.0
1.48 x 10 ⁻⁶	29.9		

The extraction of several rare earths from aqueous phases initially 1 to 2 x 10⁻⁴ M in lanthanide ion was studied as a function of pH. The resulting distribution curves are shown in Figure 1. These curves show 98 to 100% extraction of rare earths in the region pH ≥ 2.5. Although a 0.0704 M solution of HHFA in cyclohexane was a poor extractant, the large synergic effect in the presence of TBP produced nearly quantitative extraction at the lower ligand concentration. By increasing the extractant concentrations to 0.0704 M HHFA + 0.073 M TBP, 100% extraction of macro quantities of lanthanum and neodymium was obtained at pH ≥ 2.0. These data are shown in Table 5.

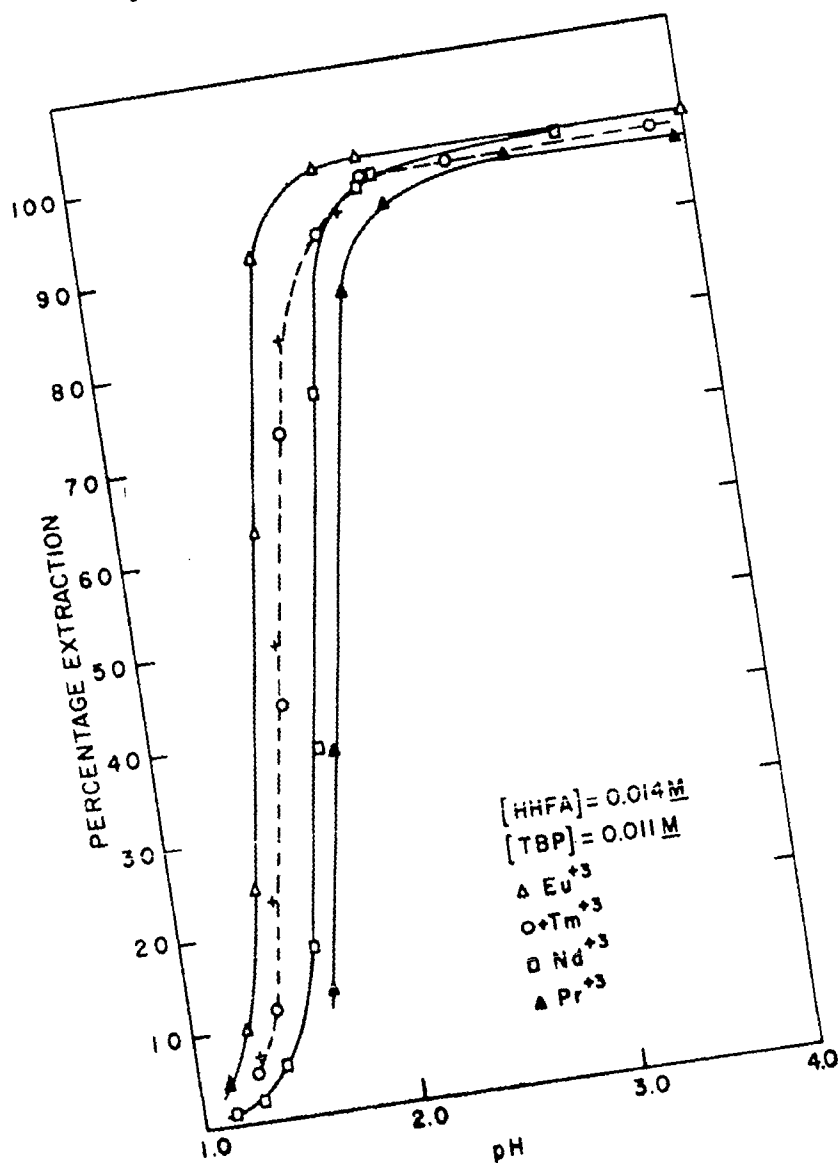


Figure 1. Distribution of lanthanides versus pH in the HHFA-TBP-cyclohexane system

Table 5. Extraction of rare earths with 0.0704 M HHFA + 0.073 M TBP in cyclohexane

1.393 x 10 ⁻³ M La(III)			1.140 x 10 ⁻³ M Nd(III)		
pH	K _D	E	pH	K _D	E
0.92	1.17	43.3	0.52	.004	0.43
1.03	1.25	55.5	0.61	.016	1.6
1.20	4.43	81.6	0.82	0.140	12.3
1.23	6.41	86.5	1.17	2.70	73.0
1.37	14.6	93.6	1.27	4.92	92.0
1.68	86.8	98.9	1.38	11.5	95.4
1.90	237	99.6	1.47	20.7	99.8
2.47	--	~100	1.87	391	~100
			2.31	3165	~100

The mass-action effect was applied to the HHFA-TBP cyclohexane system in order to determine the stoichiometry of the extracted species. A third power dependence of the distribution ratios of Pr, Nd, Eu and Tm on the equilibrium pH is shown in Figure 2. These results indicate that 3 hydrogen ions are liberated in the extraction process (90). A plot of log K_D versus concentration of HHFA is shown in Figure 3. The respective slopes, 2.9, 2.9 and 2.8 obtained from a least squares treatment of the data approach the integer 3.0 very closely. These results for the dependence of K_D on pH and [HHFA] show that acetate and chloride anions are not involved in the extraction process. The dependence of the distribution ratio on the concentration of TBP was measured at ratios

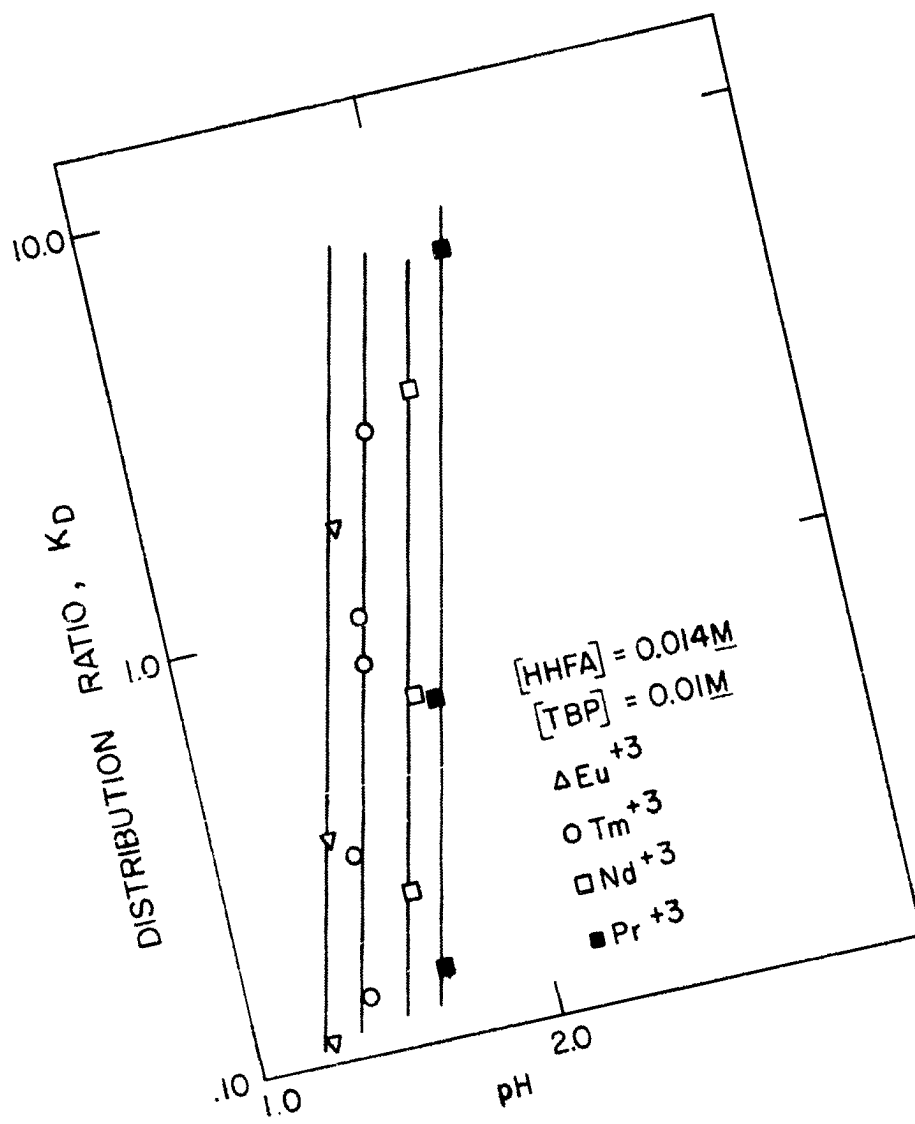


Figure 2. Dependence of the distribution ratio on pH in the HHFA-TBP-cyclohexane system

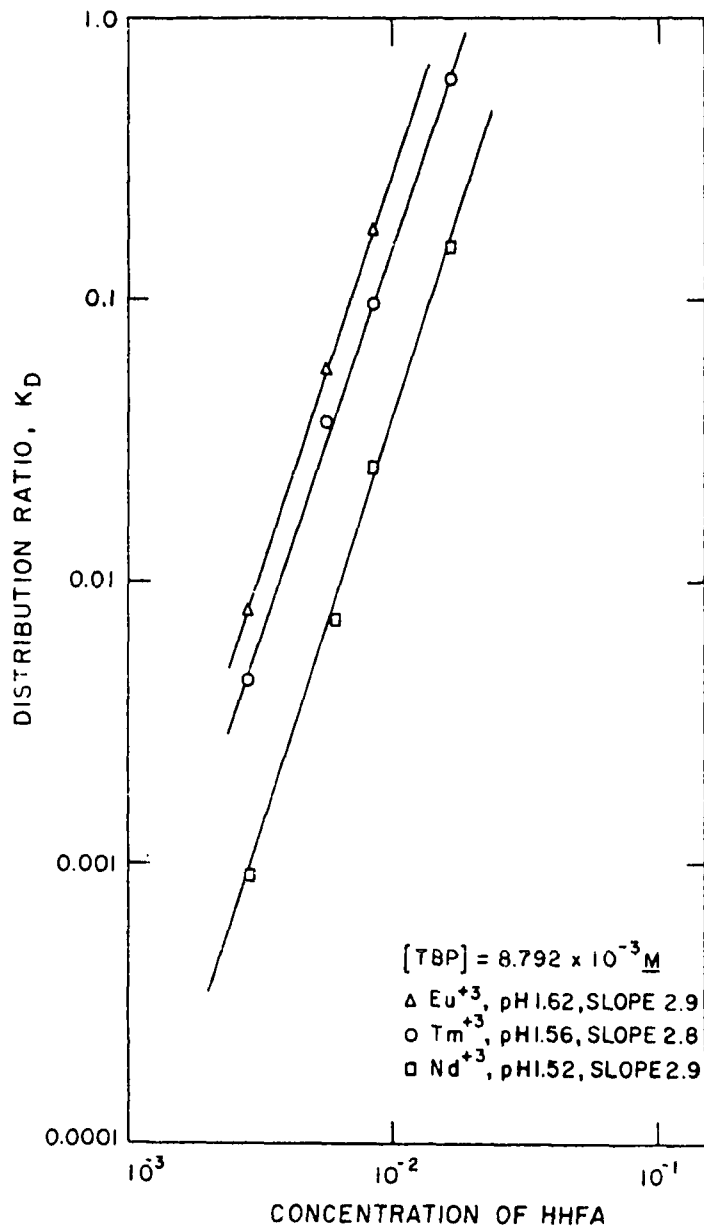
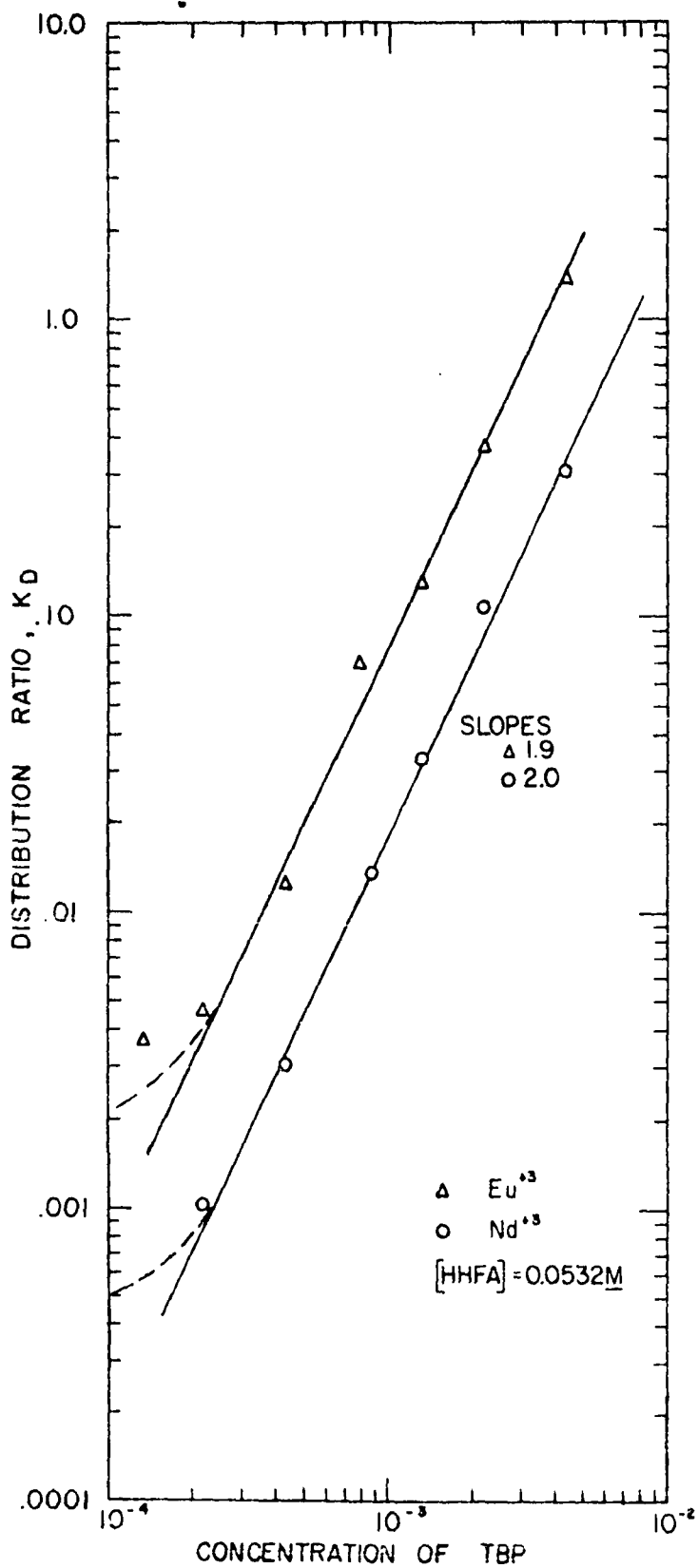


Figure 3. Dependence of the distribution ratio on the concentration of HHFA in the HHFA-TBP-cyclohexane system

of $[\text{HHFA}]/[\text{M}^{+3}]$ of 5×10^6 for Eu and 5×10^4 for Nd. These data, shown in Figure 4, indicated that 2 molecules of the donor participated in the extraction process. The slopes of plots of the TBP dependence data were not significantly altered by the addition of appropriate amounts of carrier to increase the concentrations of the cations to 1 to 2×10^{-4} M. The slopes of plots obtained at these cation concentrations and at 0.014 M ligand concentration are shown to be 1.9 in Figure 5. The data plotted in Figure 6 were obtained under similar conditions. A slope of 1.98 is shown for the TBP dependence in the region of the extraction curve which corresponds to a linear synergic effect with increasing $[\text{TBP}]_0$. The region of maximum synergism occurred at $[\text{TBP}]_0$ between 0.01 M and 0.10 M. A decrease of distribution ratios was found for $[\text{TBP}]_0 > 0.10$ M. The phenomenon of the destruction of synergism in systems containing HTTA has been systematically studied by Healy et al. (53).

The analytical significance of the results shown in Figure 6 is related to the appropriate choice of reagent concentrations for quantitative extraction of rare earths using mixtures of HHFA-TBP in cyclohexane. Although the greatest synergic effect occurred at ratios of TBP to β -diketone of

Figure 4. Dependence of the distribution ratio on the concentration of TBP in the HHFA-TBP-cyclohexane system



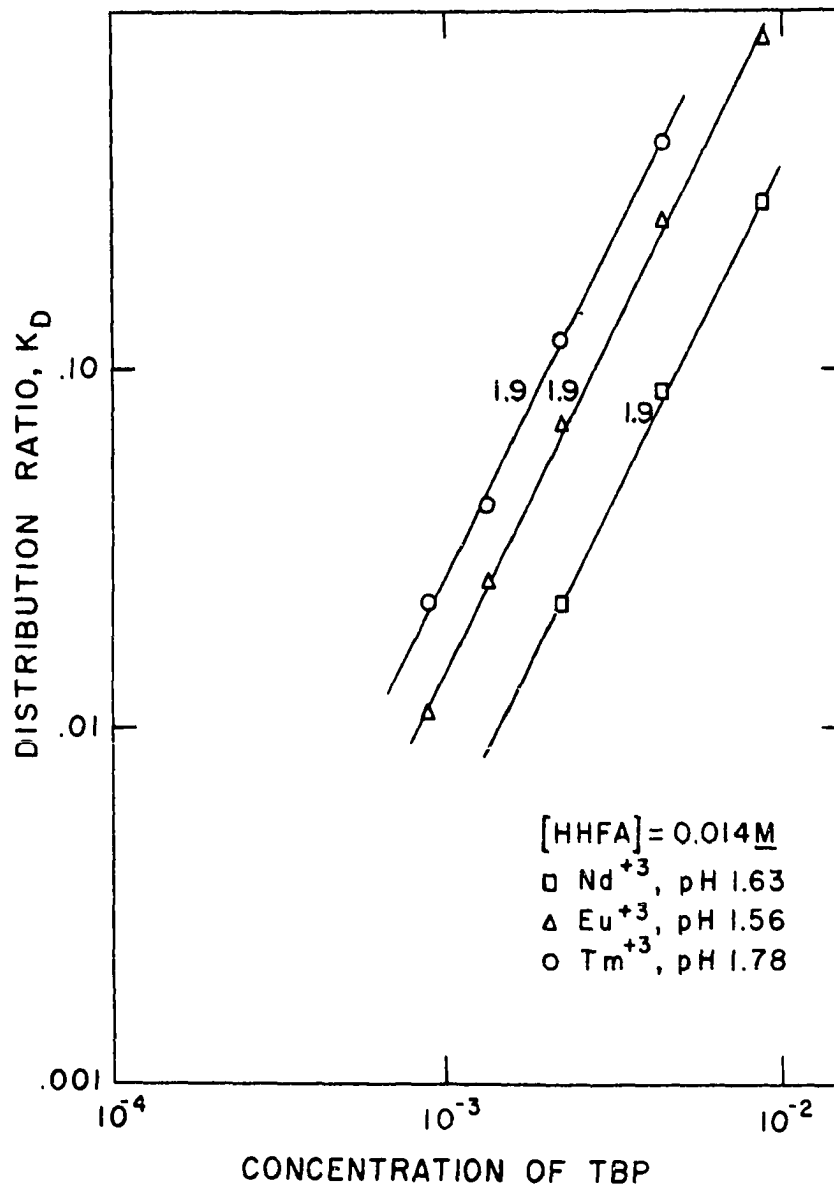


Figure 5. Dependence of the distribution ratio on the concentration of TBP in the HHFA-TBP-cyclohexane system

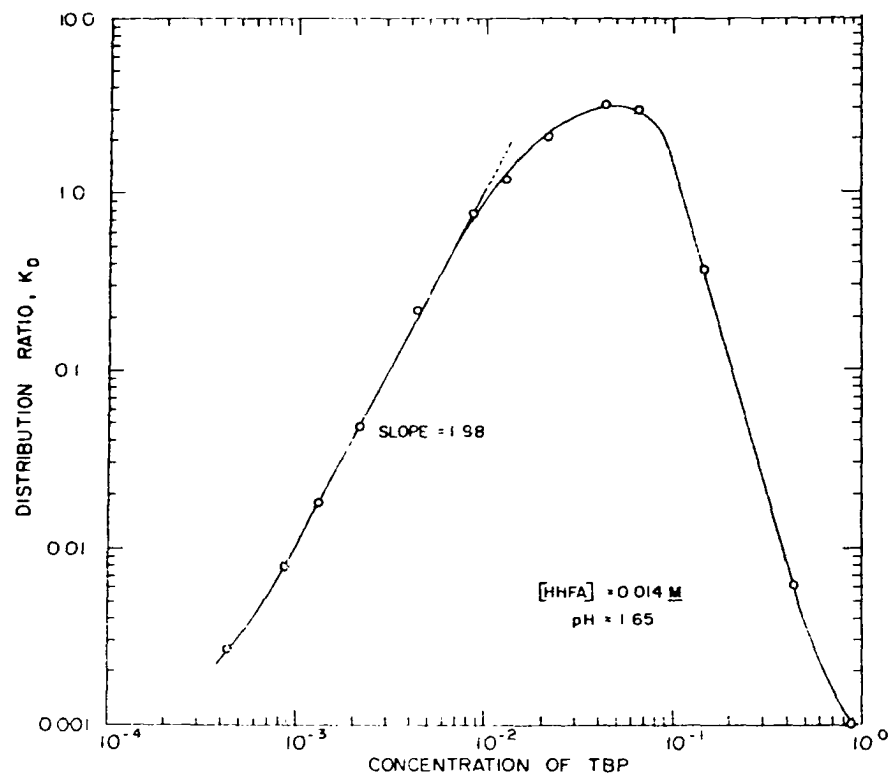
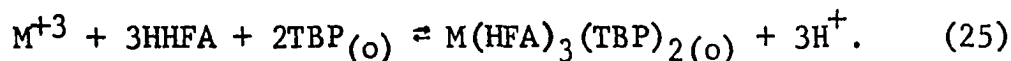


Figure 6. Destruction of synergism in the extraction of Eu by HHFA-TBP in cyclohexane

2:1, reagent ratios in the range 1:1 to 10:1 may be used for analytical applications.

The overall extraction reaction corresponding to the extraction data may be written as follows:



During the previous studies aqueous phases 10^{-4} to 10^{-8} \underline{M} in rare earth cations were employed in the determination of the composition of the extracted complexes. In analytical situations higher concentrations of cations are frequently encountered. It is therefore important to determine the concentration range over which the stoichiometry of the extracted species remains constant. In view of the negligible difference in the slopes obtained in the region $[M^{+3}] = 1$ to 2×10^{-4} \underline{M} from those obtained at $[M^{+3}] \leq 1 \times 10^{-5}$ \underline{M} , the non-constancy of the distribution ratios in the region 3×10^{-4} $\underline{M} \leq [M] \leq 1 \times 10^{-5}$ \underline{M} does not result from the extraction of species of different composition into the organic phase. Although this behavior has been observed to occur upon the formation of polynuclear cation-containing species in the aqueous phase (95), it is not likely that polymerized species containing lanthanides exist in the aqueous phase in this concentration range especially at the $[H^+]$ employed in these

studies. Decreasing distribution ratios with increasing concentration of cations is often indicative of a degree of complexation which is extensive enough to induce changes in the effective free concentrations of the organic reagents. The behavior observed at $[M^{+n}]$ above $2 \times 10^{-4} \text{ M}$ probably resulted from this effect.

The results obtained during this study at low concentrations of the rare earth, and the data reported by Butts (19) for the species extracted from 0.0125 M Eu and 0.0097 M Lu into solutions of HHFA-TBP in cyclohexane, provide evidence that the stoichiometry of the lanthanide complexes extracted from aqueous solutions 10^{-8} to 10^{-2} M in the cation corresponded to $M(\text{HFA})_3(\text{TBP})_2$.

It was also evident from these studies that several side reactions were either negligible or absent. Other investigators have reported that a neutral molecule of HTTA or HAA can function as a donor (87,92). Complexes of the composition, $L(\text{R.E.})(\text{HFA})_4$, where L is an alkali metal, have also been reported (7). The data concerning the dependence of the extraction on pH and on the concentration of HHFA obtained in this study indicated that the reactions, $M^{+3} + 4\text{HHFA} \rightleftharpoons M(\text{HFA})_3 \cdot \text{HHFA}(\text{o}) + 3\text{H}^+$ and $M^{+3} + L^{+1} + 4\text{HHFA} \rightleftharpoons L M(\text{HFA})_4(\text{o}) + 4\text{H}^+$

do not occur in the synergic system. Because of the small value of the constant, $K_T = [\text{Keto}]_{\text{HHFA},(o)} / [\text{Enol}]_{\text{HHFA},(o)}$ (18) and the decreased chelating ability of the carbonyl oxygens of the keto form of the fluorinated β -diketones, it appears that a neutral molecule of HHFA cannot compete favorably with TBP as an adduct molecule. Although mechanisms for extraction reactions cannot be deduced from equilibrium data alone, plausible reactions for the direct formation of the species,

$L M(\text{HFA})_4$, in an extraction system can be written as follows:

- 1) $L^+ + M(\text{HFA})_4^-(o) \rightleftharpoons L M(\text{HFA})_4(o)$
- 2) $L^+ + M(\text{HFA})_4^- \rightleftharpoons L M(\text{HFA})_4(o)$
- 3) $L\text{HFA}(o) + M(\text{HFA})_3(o) \rightleftharpoons L M(\text{HFA})_4(o)$
- 4) $L\text{HFA} + M(\text{HFA})_3 \rightleftharpoons L M(\text{HFA})_4(o)$

Reaction 1 can be rejected on the basis of considerations of the dielectric constant. Reaction 3 would require the extraction of the alkali metal- β -diketone chelate. Healy's (50) data for the extraction of alkali metals by HTTA-TBP-benzene suggests that no extraction of sodium would occur at the low pH employed in the HHFA-TBP-cyclohexane system. Although reactions 2 and 4 could possibly occur in the absence of TBP, the strong synergic reaction between the neutral hydrated metal chelate and TBP would prevent the formation of anionic

chelate complexes in the aqueous phase and not permit the reaction of LHFA with the tris chelate to occur.

Liquid-Liquid Extraction with Trifluoroacetylacetone

Distribution curves for the extraction of several lanthanides into solutions of HTFA in benzene are shown in Figure 7. The scant extraction of lanthanides with this reagent is similar to results obtained by Brown et al. (17) during a study of the extraction of rare earths by HAA. They attributed the poor efficiency of HAA as an extractant for lanthanides to the formation of hydrates which limited the solubility of the chelates in the organic solvents. The distribution behavior observed for the chelates of HTFA is consistent with their explanation since this structurally similar ligand also forms hydrated rare-earth chelates (113).¹¹

Distribution curves for the synergic extraction of lanthanides into solutions of HTFA and TBP in cyclohexane are shown in Figure 8. It is seen that the lanthanides are quantitatively extracted at pH 3.8 where hydrolysis of these cations does not occur. The effect of the concentration of HTFA on distribution ratios is shown in Figure 9. The slopes

¹¹See discussion on thermal behavior of hydrated chelates.

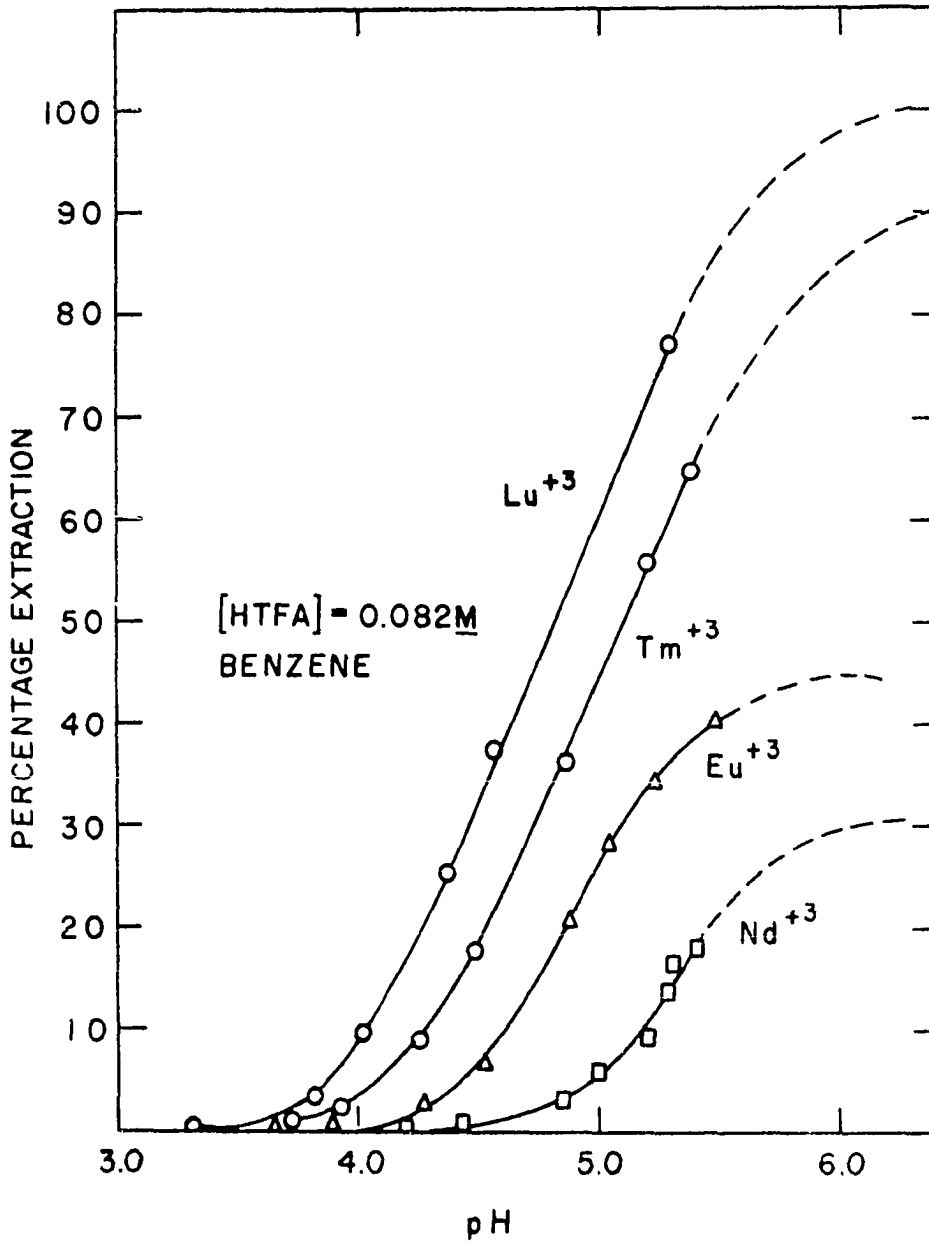


Figure 7. Extraction of lanthanides with HTFA in benzene

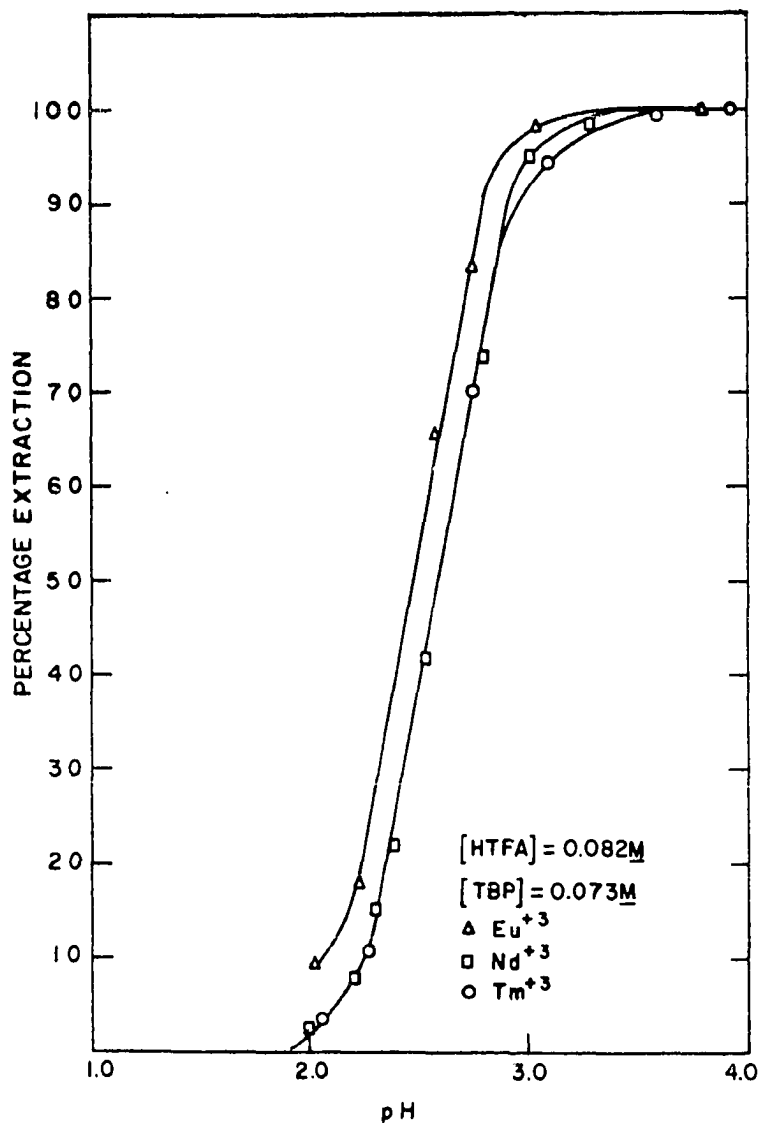


Figure 8. Extraction of lanthanide with HTFA-TBP in cyclohexane

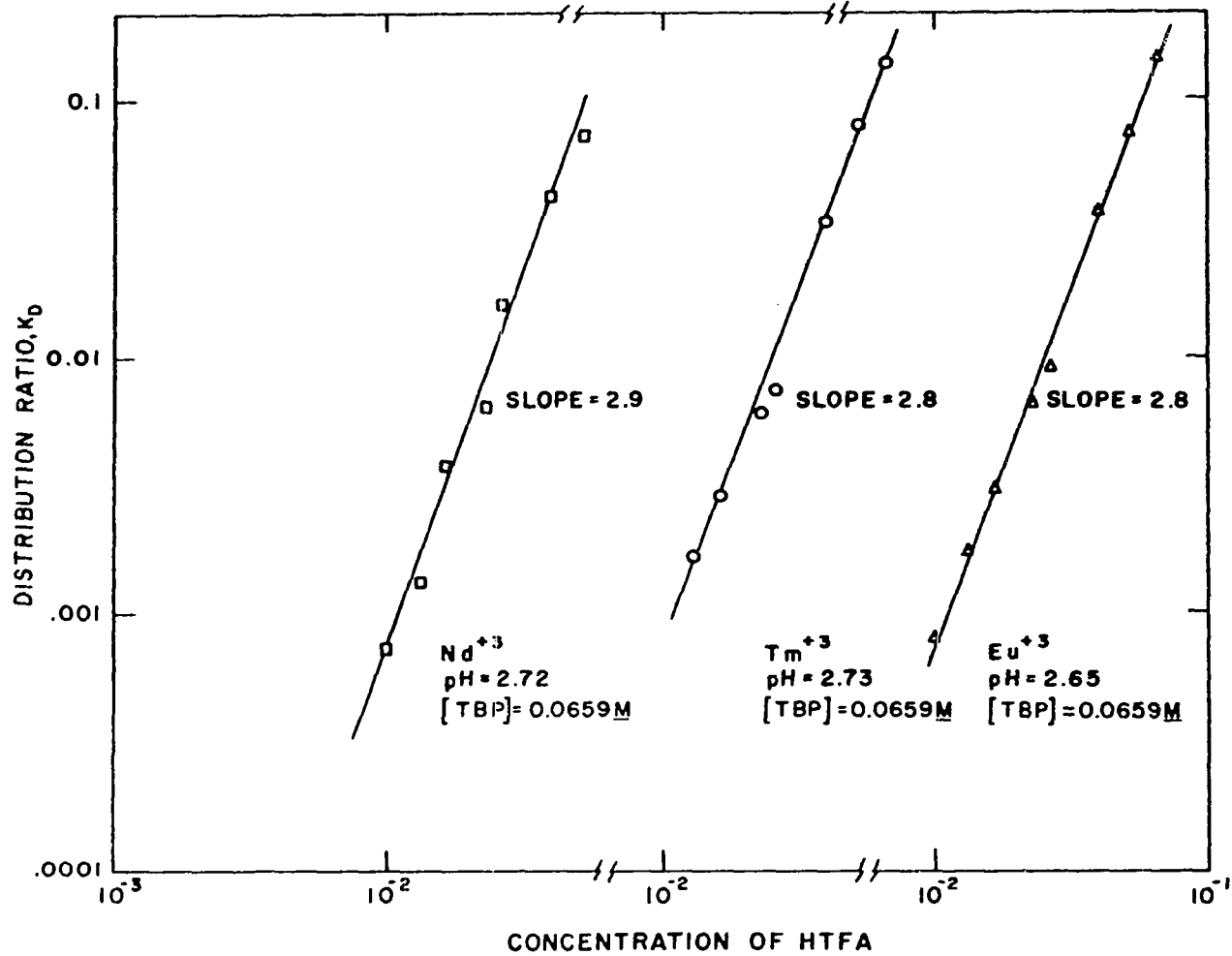


Figure 9. Dependence of the distribution ratio on the concentration of HTFA in the HTFA-TBP-cyclohexane system

obtained from a least squares treatment of the experimental data are indicative of the formation of tris chelates. Although the data shown in Figure 10 strongly indicate the predominate formation of a diadduct complex with TBP, contributions from the increased importance of a monoadduct cannot be excluded on the basis of these results.

The extraction of thulium into cyclohexane containing a constant amount of HTFA and varying molar ratios of TBP to Tm(III) was studied. The mole ratio data reported in Figure 11 showed the formation of the monoadduct and confirmed its conversion to the diadduct complex.¹² These results indicate that the extraction process in the HTFA-TBP-cyclohexane system is represented by the overall reaction,



Liquid-Liquid Extraction with 8,8,8,7,7,6,6-heptafluoro-2,2-dimethyl-3,5-octanedione (HFOD)

Rare earth cations were found to be appreciably extracted into benzene solutions of HFOD. The distribution curves shown in Figure 12 indicate that all rare earths can be extracted

¹²A discussion of the mole ratio method is presented in the section on HFOD extractions.

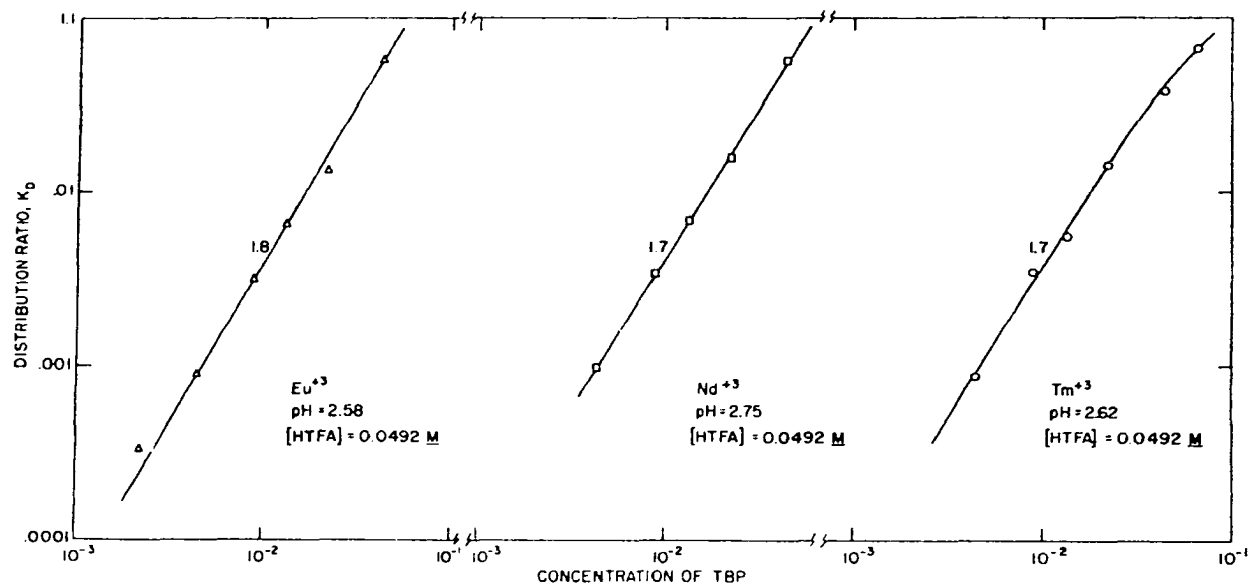


Figure 10. Dependence of the distribution ratio on the concentration of TBP in the HTFA-TBP-cyclohexane system

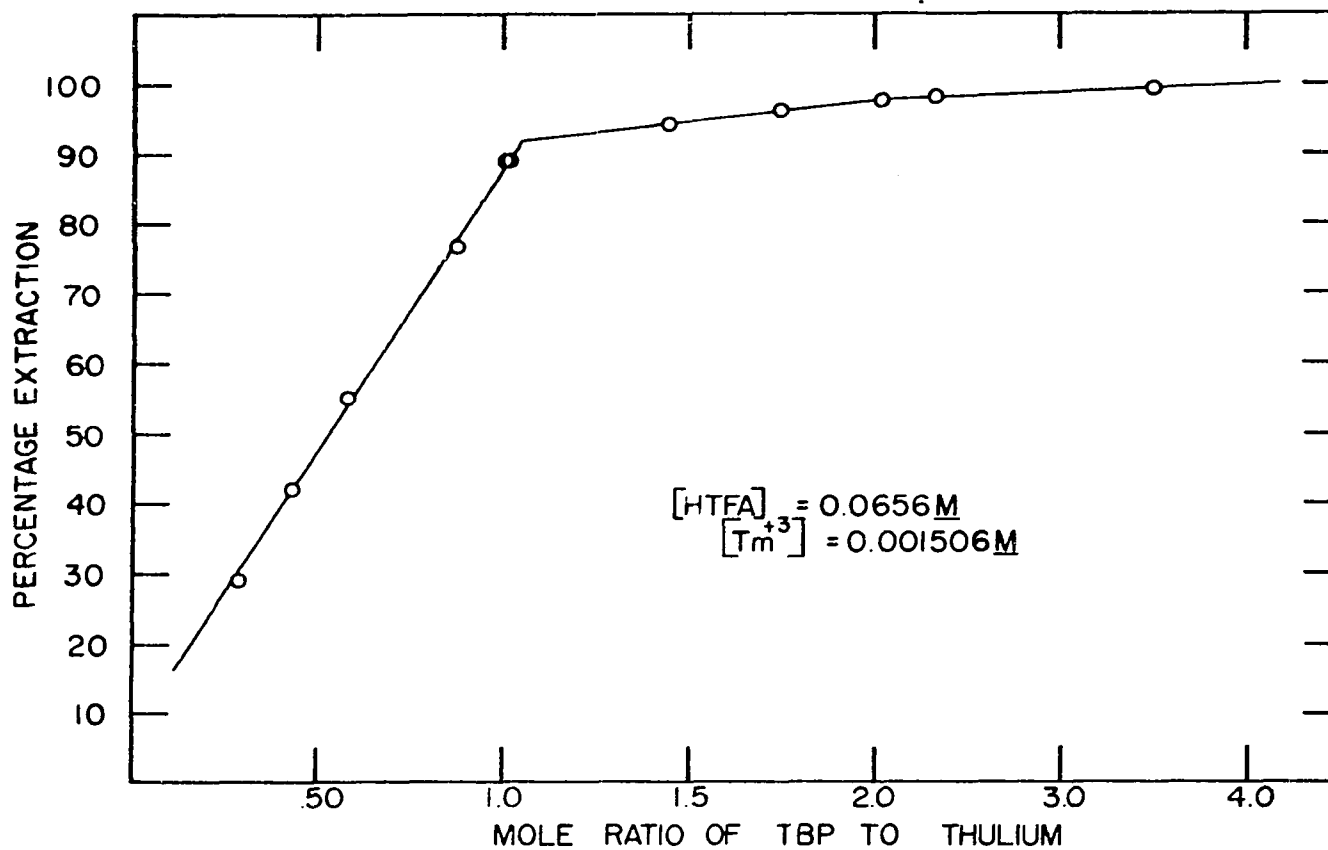


Figure 11. Dependence of the extraction of Tm^{+3} on the mole ratio, $[TBP]_0/[Tm^{+3}]_{initial}$, in the system HTFA-TBP-cyclohexane

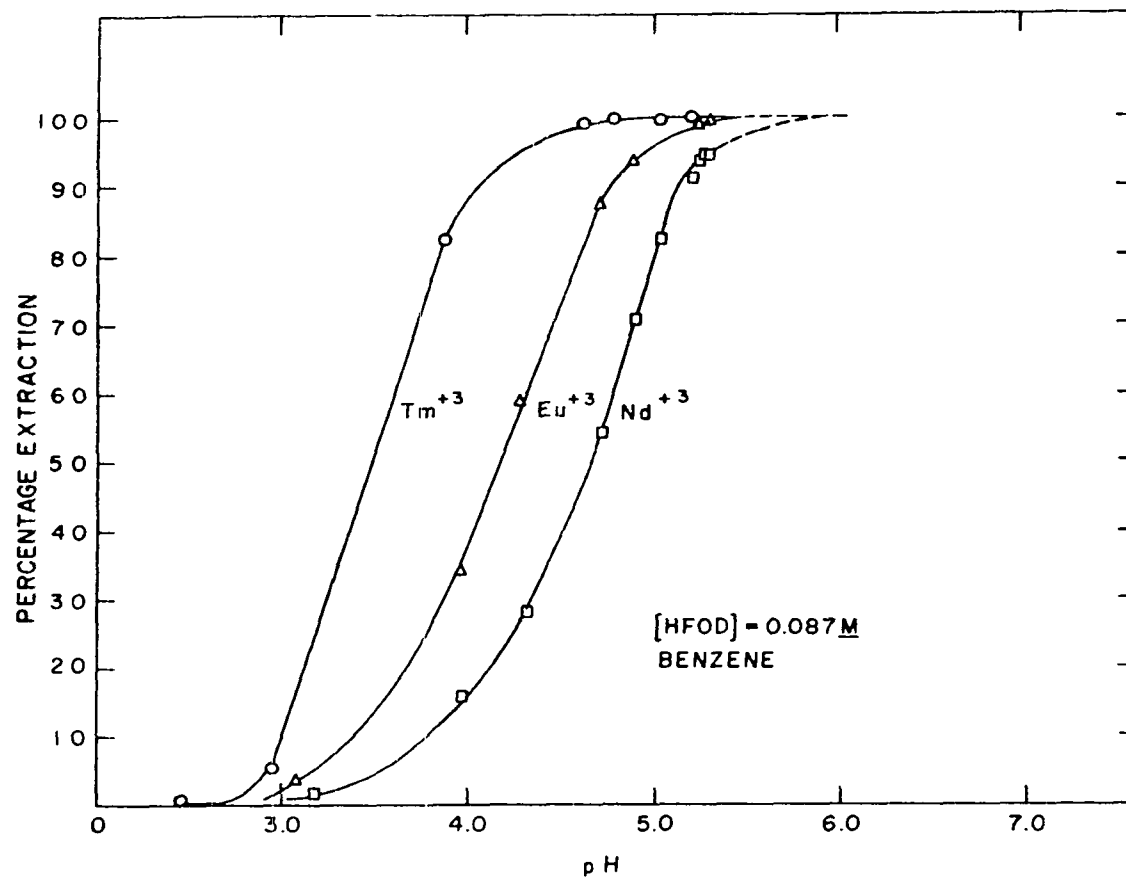


Figure 12. Extraction of lanthanides with HFOD in benzene

at $\text{pH} \geq 6.0$. The improvement in the extraction of lanthanides by this ligand over that exhibited by HHFA or HTFA resulted from the larger partition coefficients of chelates of HFOD. Springer *et al.* (116) reported that rare earth chelates of HFOD contain only one mole of weakly bonded water. In contrast chelates of HHFA and HTFA are strongly bonded to 2 or 3 water molecules. The observed increase in the extraction of rare earths by HFOD is consistent with a decreased tendency for hydrate formation which leads to an increase in the solubility of the chelates of this ligand in organic solvents.

Sievers (112) suggested that the weakly held water of hydration of R.E.-HFOD chelates was hydrogen bonded to some site on the HFOD ligand rather than being directly coordinated to the metal cation. He felt that steric crowding of the HFOD ligand restricted the maximum coordination number of the rare earths to six. The latter contention is not correct since evidence for the synergic effect in the HFOD-TBP-cyclohexane system was obtained during this research. The distribution curves for the extraction of rare earths into solutions of HFOD and TBP in cyclohexane are shown in Figure 13. The displacement of these extraction curves to a lower pH region than is observed for extractions with HFOD alone¹³ is char-

¹³See Figure 12.

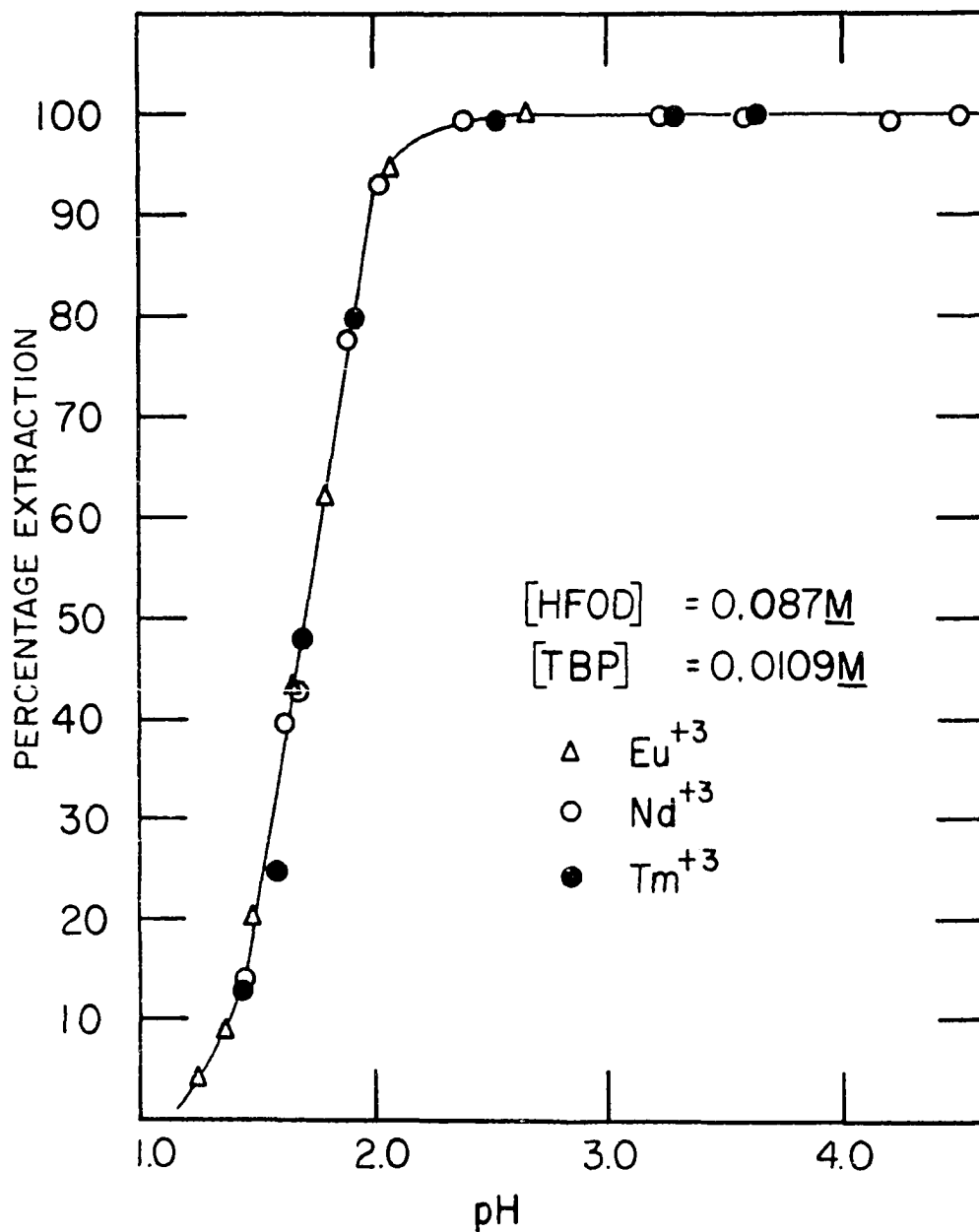
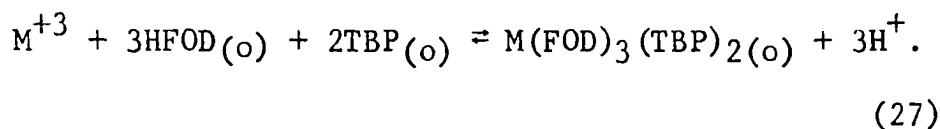


Figure 13. Extraction of lanthanides with HFOD and TBP in cyclohexane

acteristic of the synergic effect and indicative of the participation of TBP in the extraction process. One hundred percent extraction of rare earths at $\text{pH} \geq 2.5$ is demonstrated by these data. The dependence of the distribution ratios on concentration of the HFOD is plotted in Figure 14. These data show the formation of the tris chelate. The dependence data plotted in Figures 15 and 16 clearly show the participation of TBP in the extraction reaction. The slopes of the linear portion of the plots in Figure 15 show the formation of the diadduct complex. The curvature at high [TBP] corresponds to the initiation of the destruction of synergism. The slope, 1.7, obtained for europium could result from the extraction of a mixture of the monoadduct and diadduct complexes, however this behavior was not observed for thulium which has a smaller ionic radius.

The reaction corresponding to slope data obtained by the application of the mass action effect to the extraction of trace quantities of rare earths ($[\text{Nd}] = 2.96 \times 10^{-6} \text{ M}$, $[\text{Eu}] \sim 10^{-8} \text{ M}$, $[\text{Tm}] = 2.60 \times 10^{-6} \text{ M}$) with HFOD-TBP mixtures in cyclohexane may be written as:



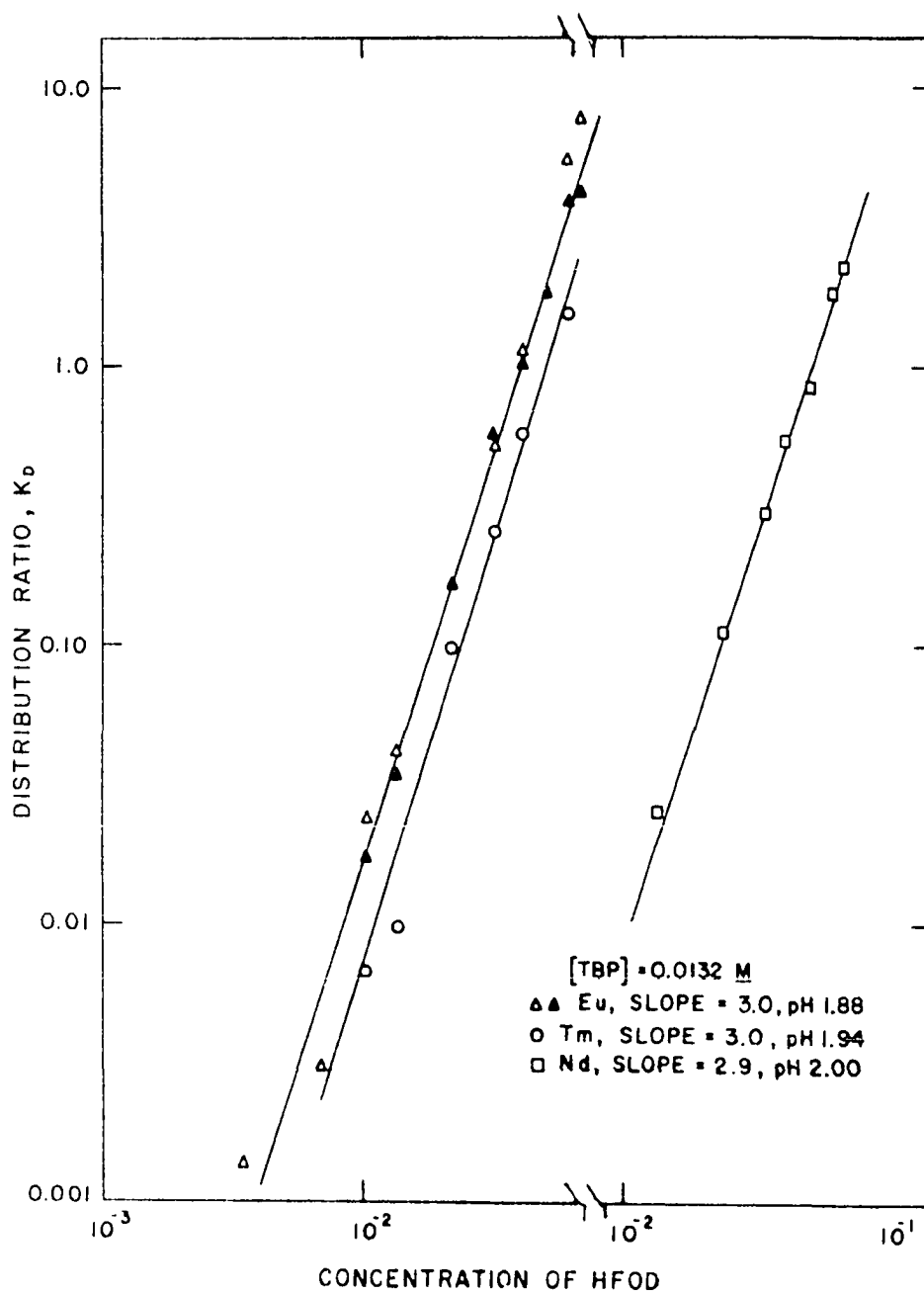


Figure 14. Dependence of the distribution ratio on concentration of HFOD in the system, HFOD-TBP-cyclohexane

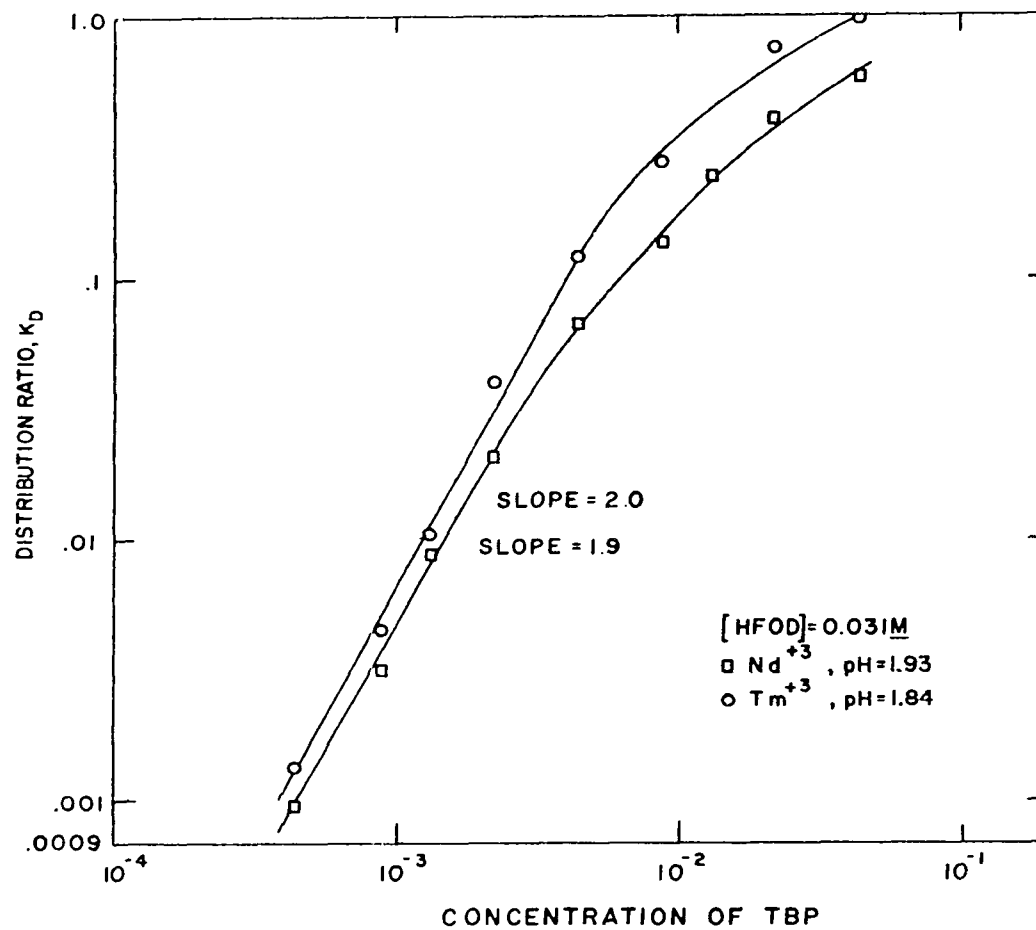


Figure 15. Dependence of the distribution ratio on concentration of TBP in the system, HFOD-TBP-cyclohexane

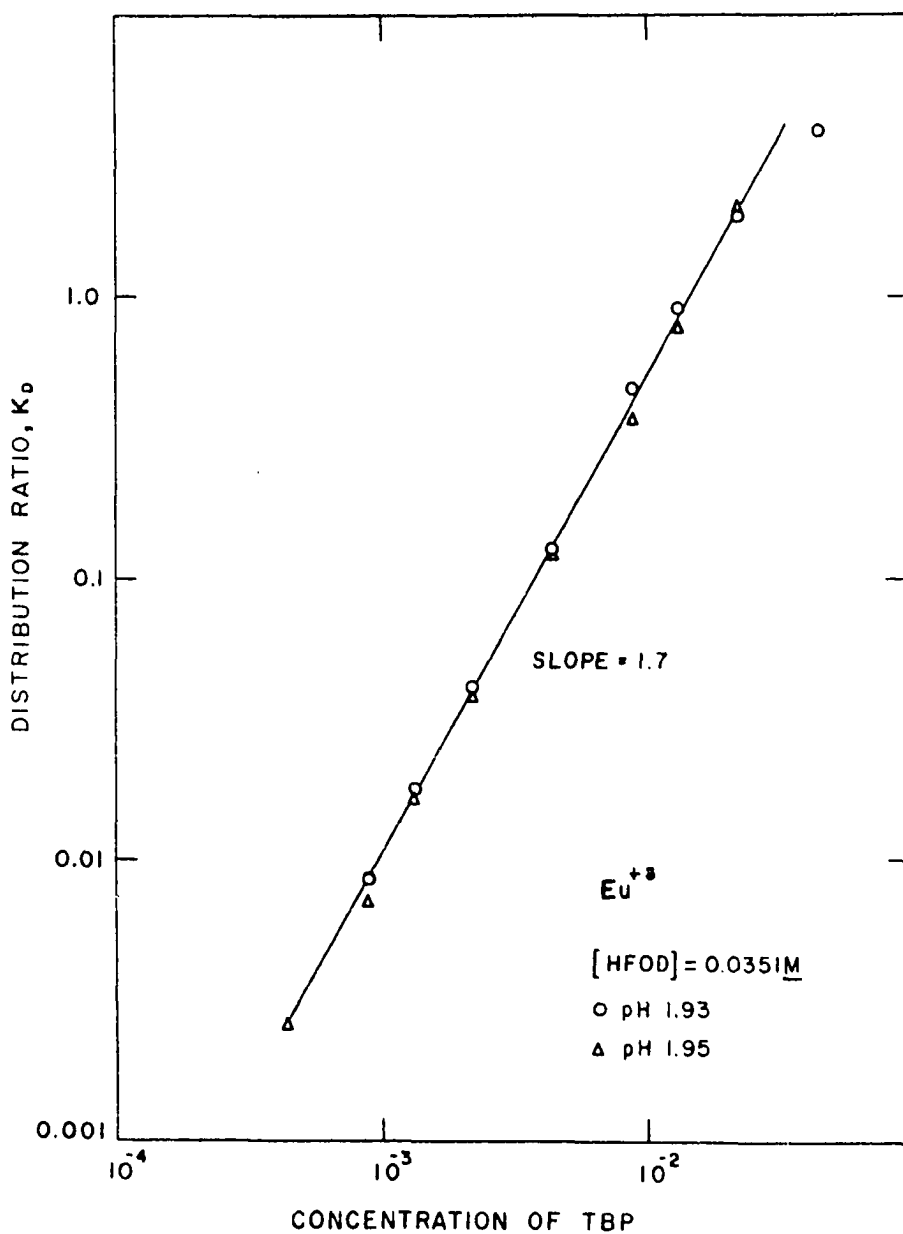


Figure 16. Dependence of the distribution ratio of Eu(III) on the concentration of TBP in the system, HFOD-TBP-cyclohexane

Mole-Ratio Study of the Extraction of Rare Earths with
Mixtures of HFOD and TBP

A mole-ratio method was used to determine the composition of the mixed HFOD-TBP complexes extracted from solutions initially 0.01 M in rare earths. The experiments performed here were similar to those methods previously described by Cary (22). At high concentrations of metal the stoichiometry of the reaction, $M^{+n} + nHFOD_{(o)} + mTBP_{(o)} \rightleftharpoons M(FOD)_n(TBP)_m_{(o)} + nH^+$, can be deduced by monitoring the percentage of cation extracted as the molar ratio of reagent to metal is varied. The percentage of cations extracted from aqueous phases buffered with acetate into cyclohexane containing a constant amount of TBP and different mole ratios of HFOD to rare earth was determined by tracer techniques for Eu and Tm. The extent of extraction of Nd and Ho was determined by measuring the absorbance of the mixed complex in the organic phase. The data in Figure 17 show 100% extraction at mole ratios of ligand to metal of 3 to 1. The absence of acetate and chloride anions in the extraction reaction is confirmed by the formation of the tris chelate. Mole-ratio data for TBP with Pr, Nd, Eu and Tm are shown in Figures 18 and 19. The changing slope of these plots of absorption data show the formation

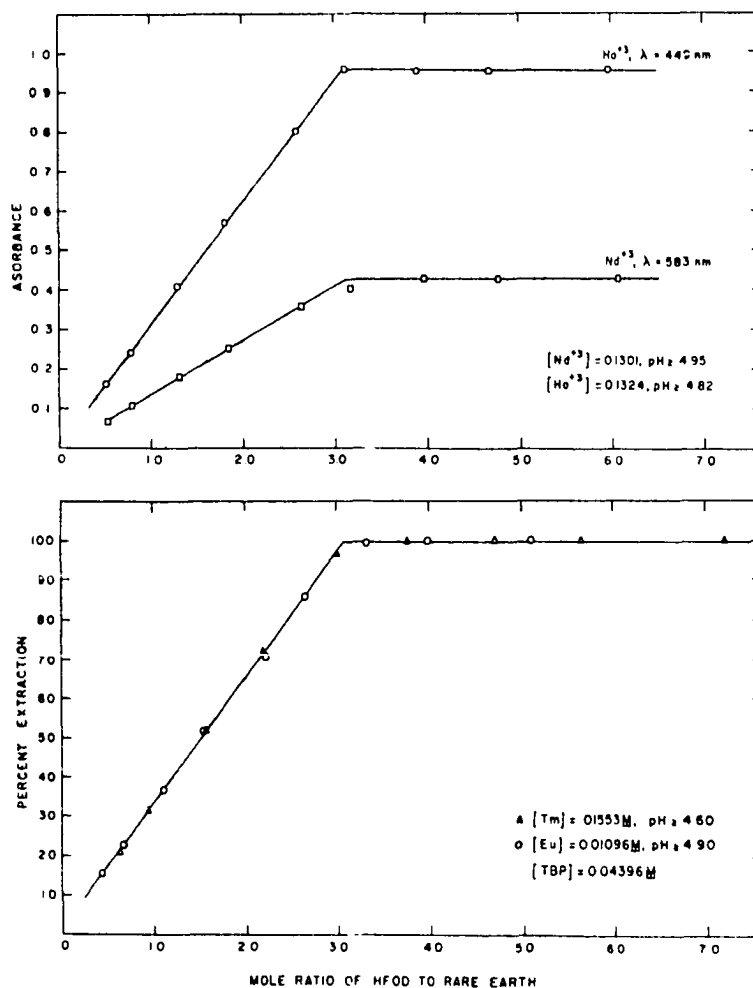


Figure 17. Dependence of the extraction of lanthanides on the mole ratio, $[\text{HFOD}]_0/[\text{R.E.}]_{\text{initial}}$, in the system HFOD-TBP-cyclohexane

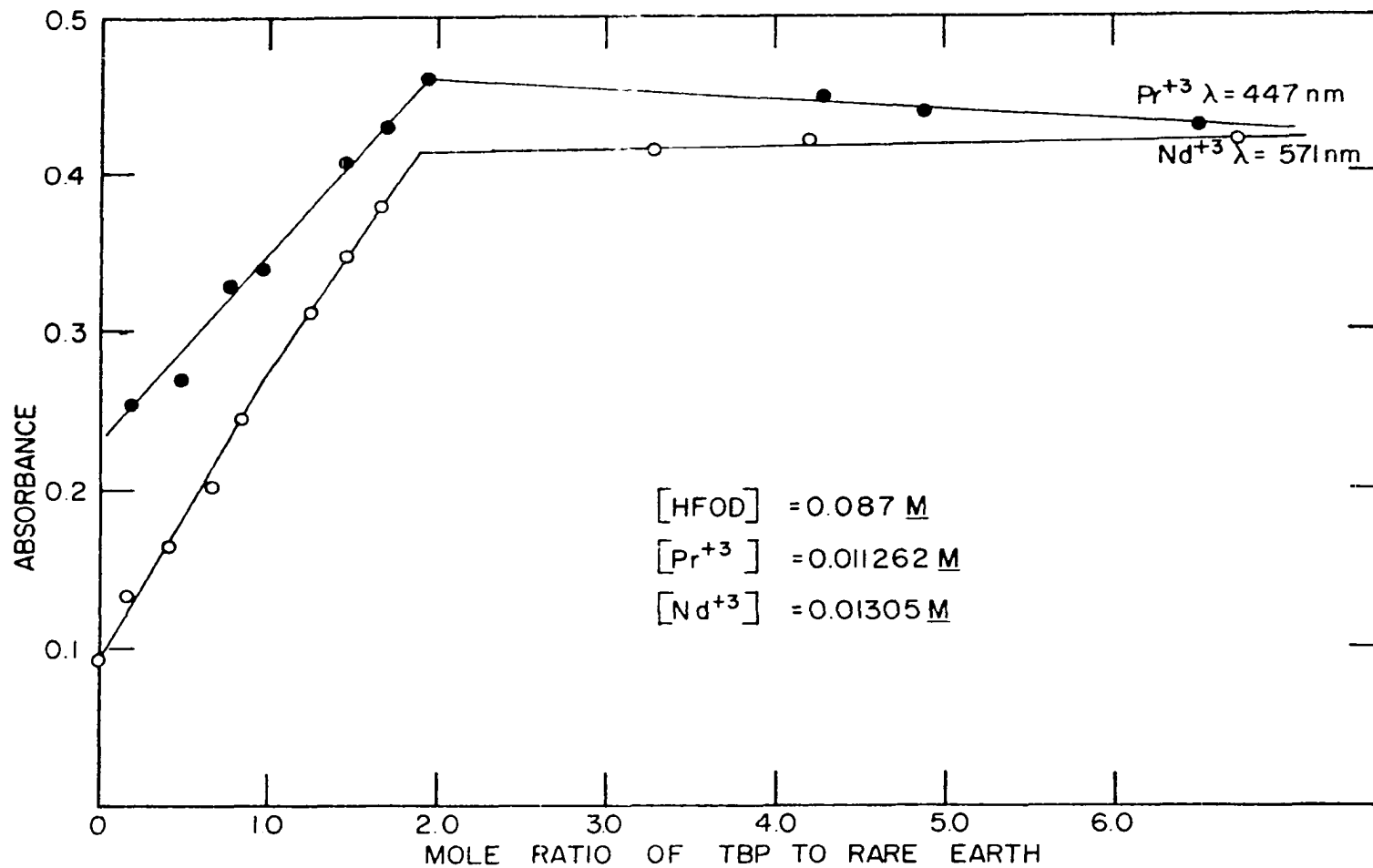


Figure 18. Dependence of the absorbance of the organic phase on the mole ratio, $[HFOD]_o/[R.E.]_{initial}$, in the system, HFOD-TBP-cyclohexane

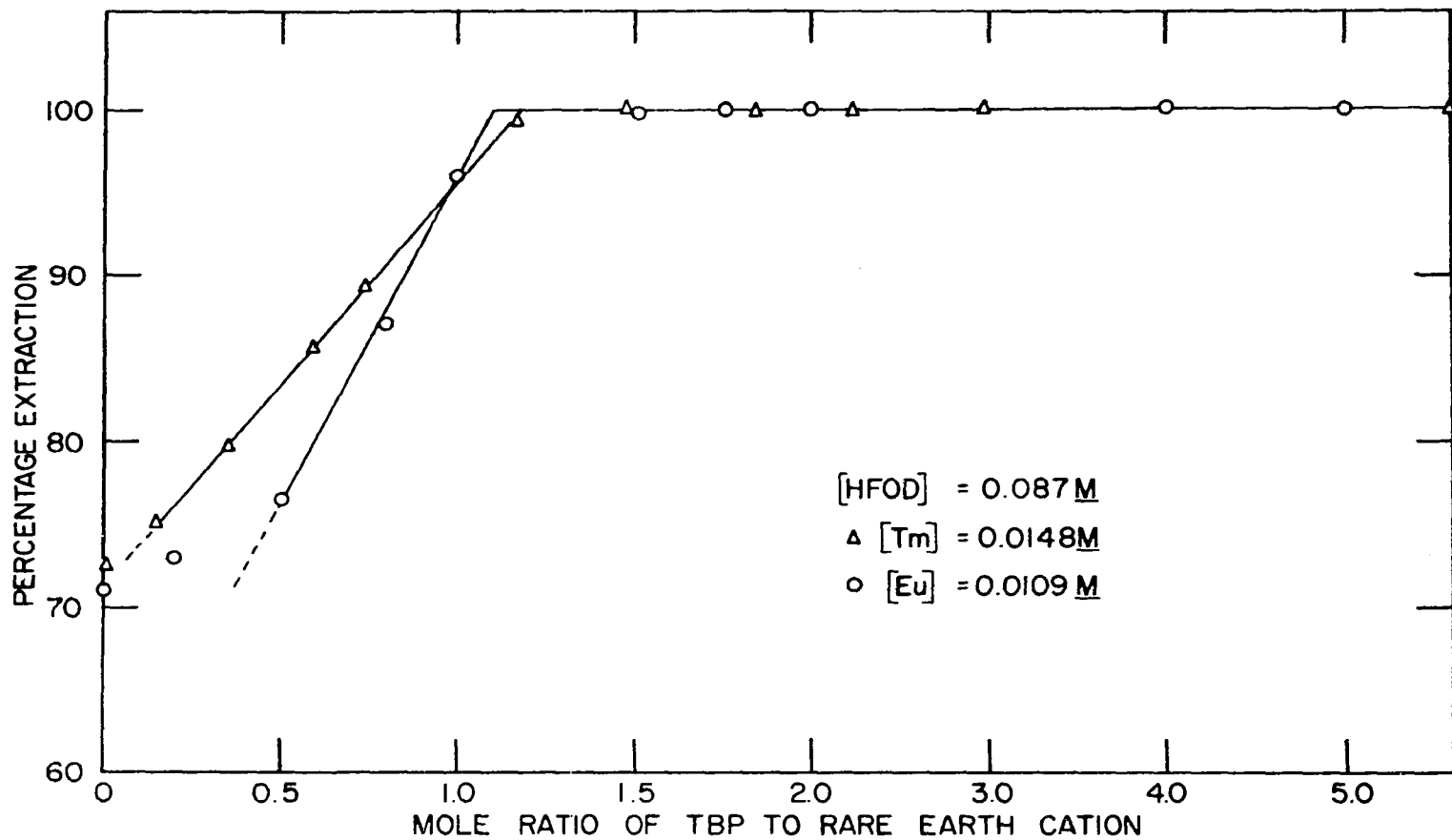


Figure 19. Dependence of the extraction of R.E. on the mole ratio, $[TBP]_o/[R.E.]_{initial}$, in the system, HFOD-TBP-cyclohexane

of the diadduct complexes of Pr and Nd. The percentage of extraction of Eu and Tm versus mole ratios of TBP to rare earth showed that the maximum extraction occurred at ratios nearly equal to 1 to 1. These extraction data do not exclude the formation of the diadduct complexes. Li et al. (71) have shown that the solubilities of mixed chelates involving HTTA and TBP or HTTA and TOPO in organic solvents are considerably larger than the chelates of the corresponding β -diketones. Since 71 to 72% of the Eu and Tm cations are extracted by HFOD alone, the increase in partition coefficients of the chelates which occurred upon displacement of the single water of hydration by a TBP molecule was sufficient to produce complete transfer of the chelate to the organic phase at 1 to 1 TBP to metal ratios. Additional adduct formation would therefore not be detected by measuring the percentage of extraction.

The enhancement of the absorption of rare earths upon coordination is well known (115,121,122). Because the ligand environment of a rare earth cation is changed upon coordination of the chelate to neutral donors, certain hypersensitive transitions of the cations should vary continuously with chemical bonding to TBP. The absorbance was measured as a function of the mole ratio of TBP to metal for Ho and Er to obtain more conclusive data for determining the composition of the

HFOD-TBP-R.E. complexes. The data in Figure 20 clearly show the existence of the monoadduct complex for both cations. The decrease in the absorbance of the organic phase for holmium at TBP to Ho mole ratios greater than 1 to 1 and the subsequent change in slope near 2 to 1 indicates the formation of the diadduct complex. Similar results were reported by Taketatsu and Banks (121) during a study of the Ho-HTTA-TOPO complex. Although the entire lanthanide series was not studied, these mole-ratio studies suggest that rare earths, up to atomic number 67, form complexes of the type R.E.(FOD)₃·2TBP. The weak tendency for the formation of diadducts at low TBP to cation ratios for lanthanides above Ho could result from the cooperative action between steric hinderance by the bulky HFOD ligand and the lanthanide contraction. These results were compared to those of a previous investigator (130) who studied the extraction of rare earths with di(1,1,3,3-tetramethylbutyl) phosphoric acid. He found that TOPO and dibutyl butyl phosphonate formed monoadducts with rare earths of atomic number <64. No synergism was detected for the heavy rare earths.

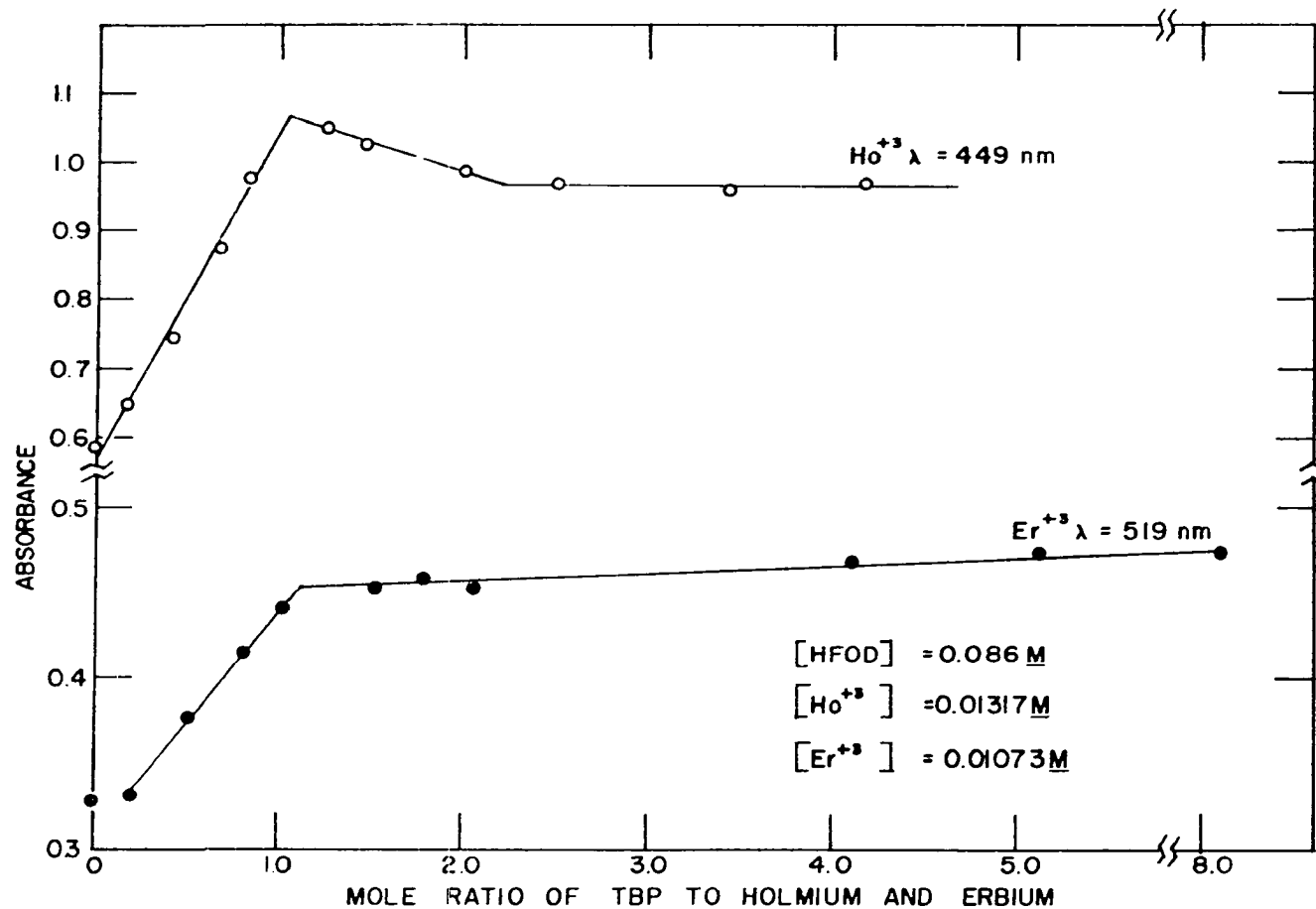


Figure 20. Dependence of the absorbance of the organic phase on the mole ratio, $[TBP]_o/[R.E.]_{initial}$, in the system HFOD-TBP-cyclohexane

Extraction and Stability Constants of Adduct Complexes

The total equilibrium concentration of undissociated ligand, $[HA]_{T'}$, is given by the relationship

$$[HA]_{T'} = [HA]_{o,initial} - 3[M^{+n}]_{initial} (E/100) - \frac{[HA]_{o,initial}}{K_{D,HA} \{ [H]K_a^{-1} + 1 \} + [H^+]K_a^{-1} + 1}, \quad (28)$$

where $K_{D,HA}$ is the distribution ratio of the ligand HA. The second term in Equation 28 is negligible at $[HA]_{o,initial} \geq 10^3 [M^{+n}]_{initial}$. At $[H^+] \geq 10^2 K_a$ the $[A^-]$ can be considered negligible with an error of $\leq 1\%$. Equation 28 then reduces to $[HA]_{T'} = [HA]_{o,initial}$. The ligand, HA, at equilibrium is distributed between the aqueous and organic phases according to $P_{HA} = [HA]_o/[HA]$. At $P_{HA} \geq 90$ the reagent remains essentially in the organic phase and is principally distributed into the aqueous phase at $P_{HA} \leq 0.01$. The concentration equilibrium constant for the synergic extraction of cations is then given by Eq. 20 for the former case and by

$$K_{eq} = K_D [H]^3 / [HA]^3 [D]_o^2 \quad (29)$$

for the latter. Equation 29 was used to describe equilibria in systems containing HTFA, HHFA or HFHD. In the system containing HFOD Eq. 20 was found to be applicable. No correc-

tions for changes in the activity of HA resulting from self-association and hydrogen bonding to TBP were considered since Pukanic and co-workers (88) reported equilibrium constants for hydrogen bonding of HHFA and HTFA with TBP to be 1.39 and 0.20, respectively, at 37°C. These β -diketones were also shown to be monomeric in CCl_4 at concentrations of 0.3 M.

Mitamura et al. (76) studied the extraction of H_2O and HCl from highly acidic media by CCl_4 solutions containing up to 10% TBP. They reported the equilibrium constant, $\log K = -4.65$, for the reaction, $\text{H}_{\text{aq}}^+ + \text{Cl}_{\text{aq}}^- + y\text{H}_2\text{O}_{\text{aq}} + \text{TBP}_{(\text{o})} \rightleftharpoons \text{TBP} \cdot \text{H}^+ \cdot y\text{H}_2\text{O} \text{---} \text{Cl}^-_{(\text{o})}$. In view of their data, complexation of TBP by hydration and extraction of HCl is not important under the conditions employed in these studies. Alcock and co-workers (2) have shown that the distribution of TBP between water and cyclohexane obeys the Nernst partition law for organic phases containing up to ~1.5% TBP (.06 M). Considering the large distribution coefficient of TBP, $P_D = 870$, and the negligible importance of the aforementioned reaction, $[\text{D}]_0$ was obtained from the expression, $[\text{D}]_0 = [\text{D}]_{0,\text{initial}} - (2E/100)[\text{M}^{+n}]_{\text{initial}}$. The expression reduces to $[\text{D}]_0 = [\text{D}]_{0,\text{initial}}$ at tracer $[\text{M}^{+n}]$.

The distribution ratios for the extraction of chelates

in the β -diketone system, K_D^o , and in the synergic system, K_D , are mathematically related to the concentration of the donor, $[D]_o$, and the stability constants for adduct formation in the organic phase. The respective expressions for the distribution ratios,

$$K_D^o = \frac{P_{MA} \beta_n [A]^n}{1 + \sum_{n=1}^n \beta_n [A]^n}$$

and

$$K_D = \frac{P_{MA} \beta_n [A]^n (1 + \sum_{m=1}^m \beta_m [D]_o^m)}{1 + \sum_{n=1}^n \beta_n [A]^n}$$

can be combined to give the relationship,

$$\log \frac{K_D}{K_D^o} = \log (1 + \sum_{m=1}^m \beta_m [D]_o^m). \quad (30)$$

Equation 30 belongs to a class of curves characterized by a general polynomial function. By using the above equation Sillén (114) introduced a curve fitting technique for the graphical determination of stability constants of adducts. A later modification was reported by Rossotti *et al.* (91). When only the monoadduct MA_3D exists in the organic phase, Eq. 30 is reduced to

$$\log \frac{K_D}{K_D^0} = \log (1 + \beta_1 [D]_0). \quad (31)$$

When both the MA_3D and MA_3D_2 complexes are formed in the organic phase, Eq. 30 becomes

$$\log K_D/K_D^0 = \log (1 + \beta_1 [D]_0 + \beta_2 [D]_0^2). \quad (32)$$

If arbitrary parameters are chosen such that $Y = (\log K_D/K_D^0)$, $V = \beta_2^{1/2} [D]_0$ and $p = \beta_1/\beta_2^{1/2}$, Eq. 32 is transformed into the general form, $Y = \log (1 + pV + V^2)$. Equation 32 can be fitted to a family of standard curves obtained by plotting $Y = \log (1 + pV + V^2)$ versus $X = \log V$. The asymptotes of Eq. 32 are $Y = \log \beta_2 + 2\log [D]_0$ as $[D]_0 \rightarrow \infty$ and $Y = 0$ as $[D]_0 \rightarrow 0$. At the intersection of the asymptotes, $Y = 0$ and $X = \log x_2$, the formation constant of the adduct, β_2 is determined from the relationship, $\log \beta_2 = -2\log x_2$ where x_2 is $[D]_0$ at the point of intersection of the asymptotes. The fit of the experimental data to a set of standard curves gives the value of p and β_1 can be obtained from $\beta_1 = p\beta_2^{1/2}$.

The distribution of Nd, Eu and Tm into solutions of HHFA in cyclohexane as a function of the concentration of TBP is shown in Figures 21 and 22. The slopes obtained from data in the linear portion of the curves for the above rare earths are 2.0, 2.0 and 2.1, respectively. The asymptotes of the exper-

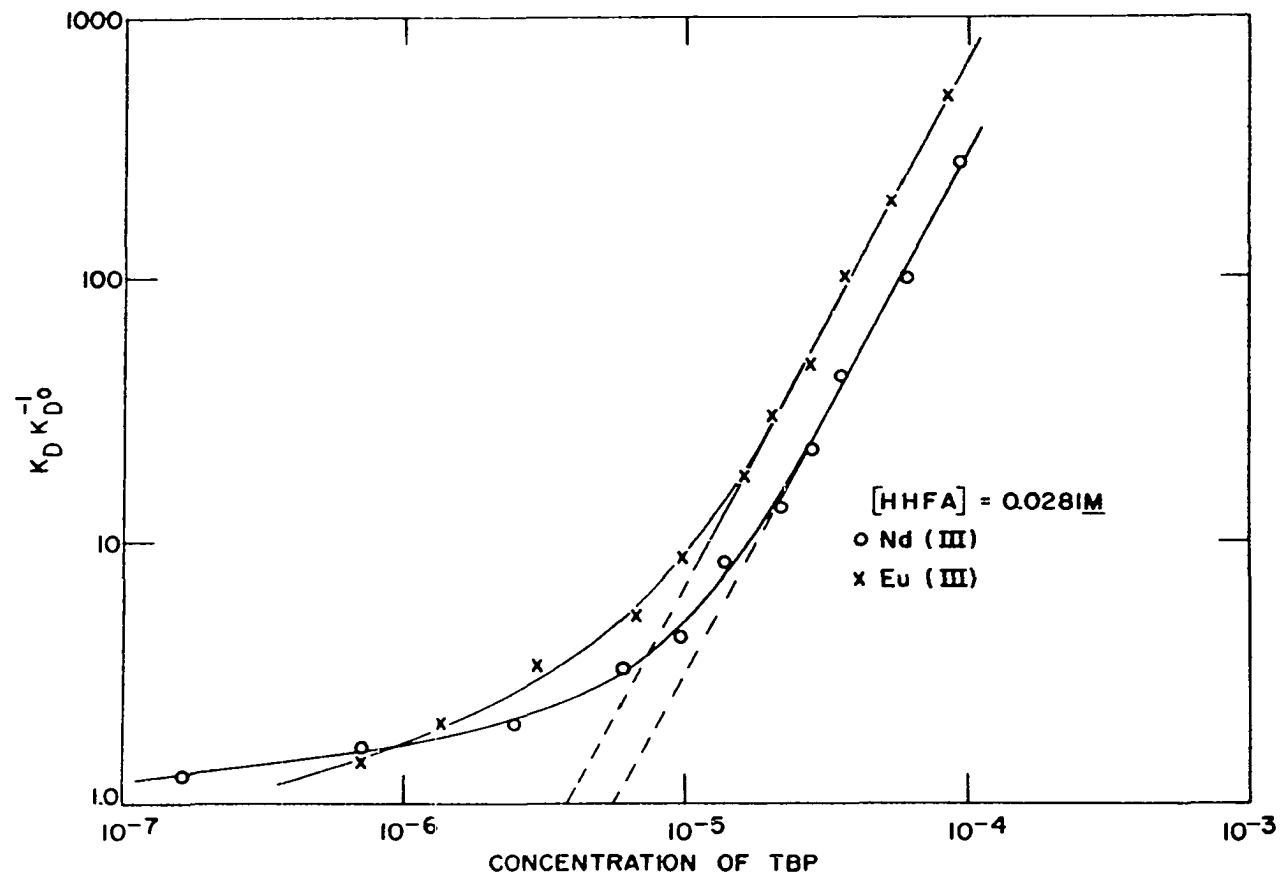


Figure 21. Dependence of the ratio, $K_D K_{D0}^{-1}$, on the concentration of TBP in the system R.E.-HHFA-TBP-cyclohexane

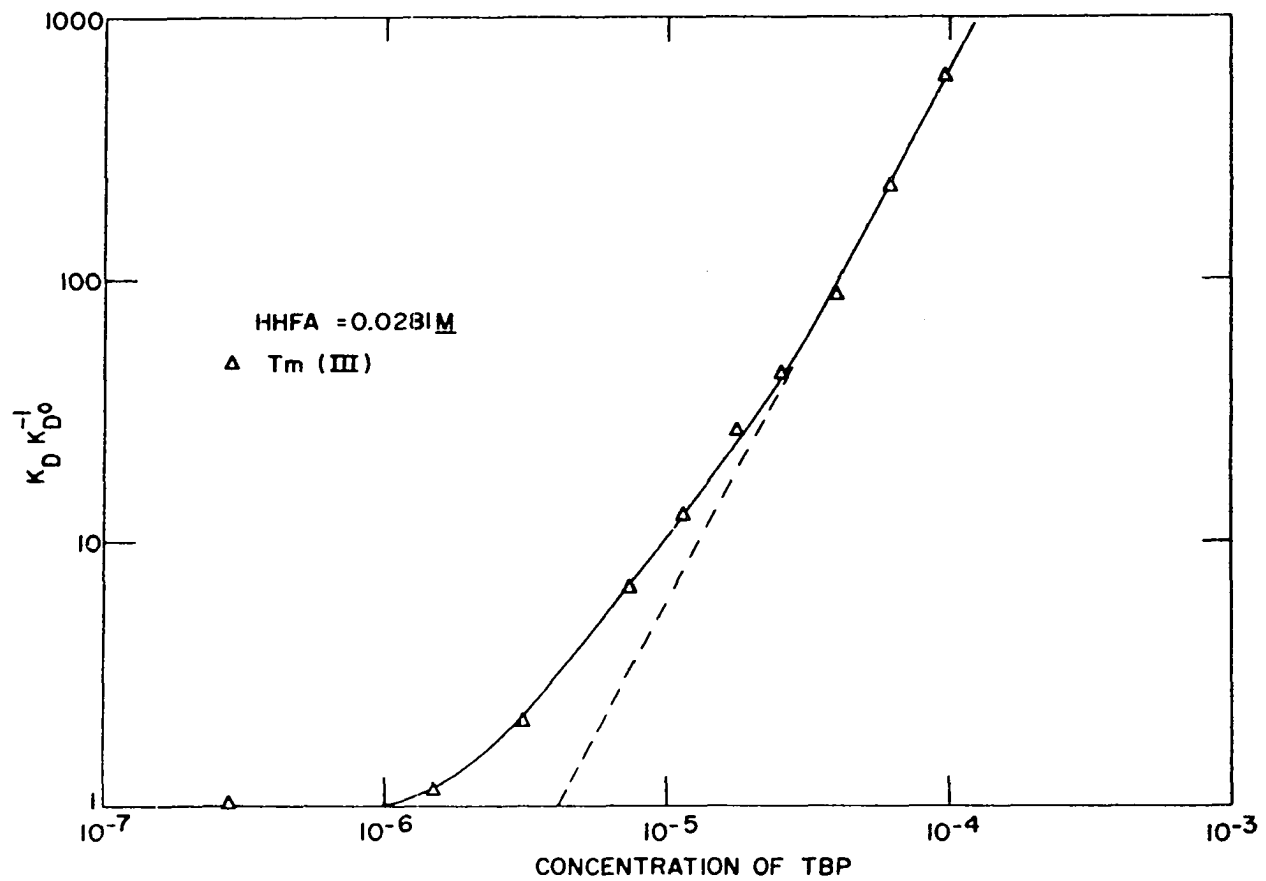


Figure 22. Dependence of the ratio, $K_D K_{D0}^{-1}$, on the concentration of TBP in the system, Tm-HHFA-TBP-cyclohexane

imental data for Nd, Eu and Tm intersect the abscissa at $\log [TBP]_O = -5.25, -5.42$ and -5.38 respectively. The stability and extraction constants for the rare earth-HHFA-TBP chelates are reported in Table 6.¹⁴

Table 6. Extraction constants for lanthanide-HHFA-TBP complexes in cyclohexane

Cation	$\log \beta_2$	$\log K_{eq}$
Nd(III)	10.50	4.346 ± 0.033
Eu(III)	10.84	5.050 ± 0.041
Tm(III)	10.76	4.627 ± 0.064

Extraction constants for the distribution of three lanthanide elements into cyclohexane containing HTFA and TBP or HFOD and TBP are given in Table 7.

Table 7. Extraction constants for R.E.-HTFA-TBP and R.E.-HFOD-TBP complexes

Cation	$\log K_{eq}, HTFA-TBP$	$\log K_{eq}, HFOD-TBP$
Nd(III)	-2.773 ± 0.061	1.644 ± 0.049
Eu(III)	-2.215 ± 0.075	1.943 ± 0.022
Tm(III)	-2.624 ± 0.140	1.735 ± 0.074

¹⁴Data for the calculation of constants may be found in the APPENDIX.

The data in Table 8 show a decrease in the synergic extraction of thulium upon substitution of TFEP and PFPP for TBP.

Table 8. Distribution of ^{170}Tm into 0.0704 M solutions of HHFA in cyclohexane containing fluorinated phosphates

HHFA-0.023 M PFPP			HHFA-0.032 M TFEP		
pH	K_D	E	pH	K_D	E
1.10	2.35×10^{-4}	0.02	1.19	7.45×10^{-4}	0.07
1.63	4.66×10^{-3}	0.46	1.92	0.0105	1.04
2.09	0.013	1.27	2.25	0.0512	4.87
2.37	0.0692	6.47	2.52	0.385	27.8
2.97	5.042	83.5	3.18	30.7	96.9
3.45	13.68	93.2	3.62	188	99.5
4.28	214.9	99.5	4.37	360	99.7
			4.63	675	99.9

A good mass balance was obtained in the system containing HHFA and TFEP. The non-constant total tracer activity found during extraction with HHFA-PFPP in cyclohexane and the formation of small droplets of a third phase indicated a decrease in solubility of the adduct complex with an increase in the fluorocarbon chain length of the donor. The solubility of the fluorinated phosphates in cyclohexane were found to be considerably less than that of TBP which appears to be miscible in all proportions. Saturated solutions of the fluorinated phosphates were obtained at concentrations of 0.03 to 0.04 M.

The smaller synergic effect with TFEP most likely resulted from the decreased solubility of the fluorinated phosphate and the corresponding adduct complex in the organic phase.

The plot for Nd(III) shown in Figure 23 has an asymptote with slope 2.0. The extraction constant, $\log K_{eq} = -0.260 \pm 0.030$ and stability constant, $\log \beta_2 = 5.87$, were obtained for the Nd(III)-HHFA-TFEP complex.

Plots of $\log K_D/K_D^0$ versus $\log [TBP]_O$ for the extraction of lanthanides into solutions of HFHD in cyclohexane are shown in Figures 24, 25, and 26. Slopes of 2.0, 2.1 and 2.1, were obtained for Nd(III), Eu(III) and Tm(III), respectively. The stability constants obtained from the respective values, -4.98, -5.00 and -5.10 of $\log [TBP]_O$ and the extraction constants calculated from data in the linear region of the extraction curves are shown in Table 9.

Table 9. Extraction constants for lanthanide-HFHD-TBP complexes in cyclohexane

Cation	$\log \beta_2$	$\log K_{eq}$
Nd(III)	9.96	9.948 ± 0.039
Eu(III)	10.00	11.058 ± 0.048
Tm(III)	10.20	10.477 ± 0.020

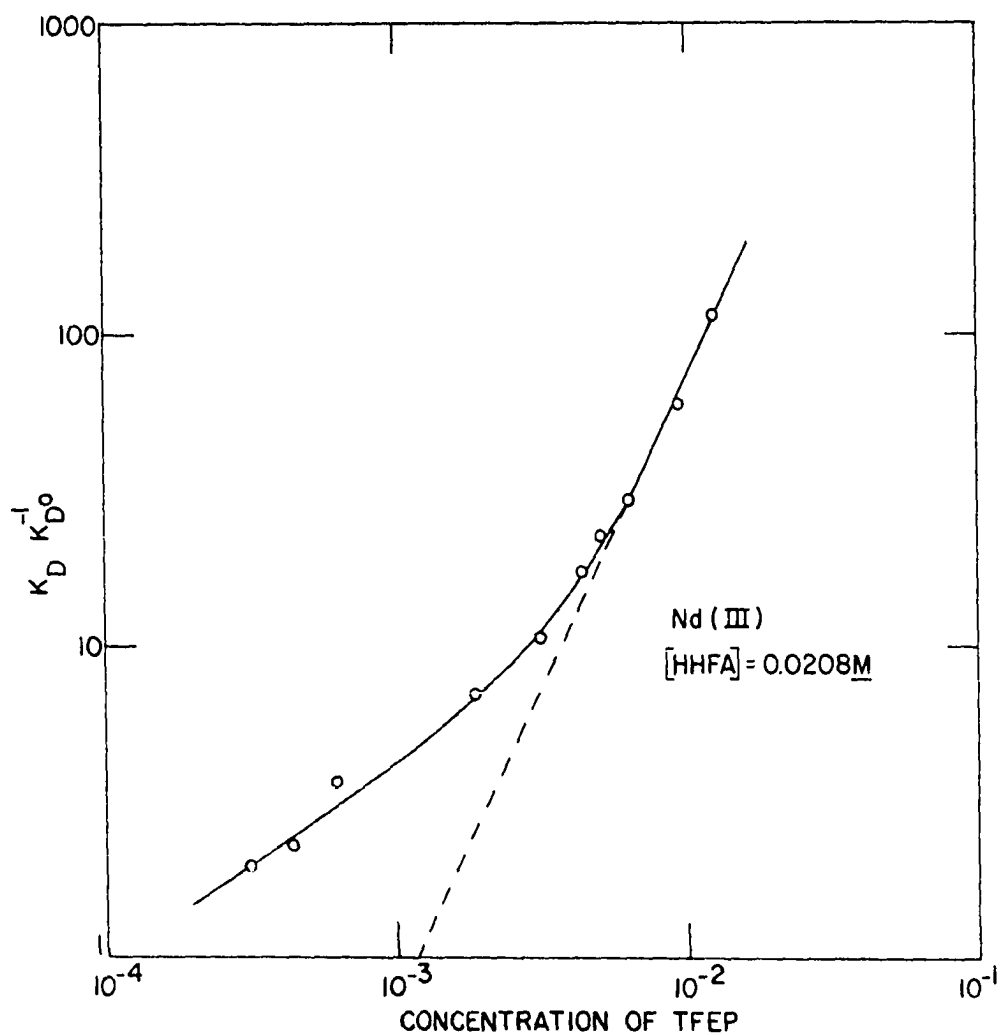


Figure 23. Dependence of the ratio, $K_D K_{D^0}^{-1}$, on the concentration of TFEP in the system, HHFA-TFEP-cyclohexane

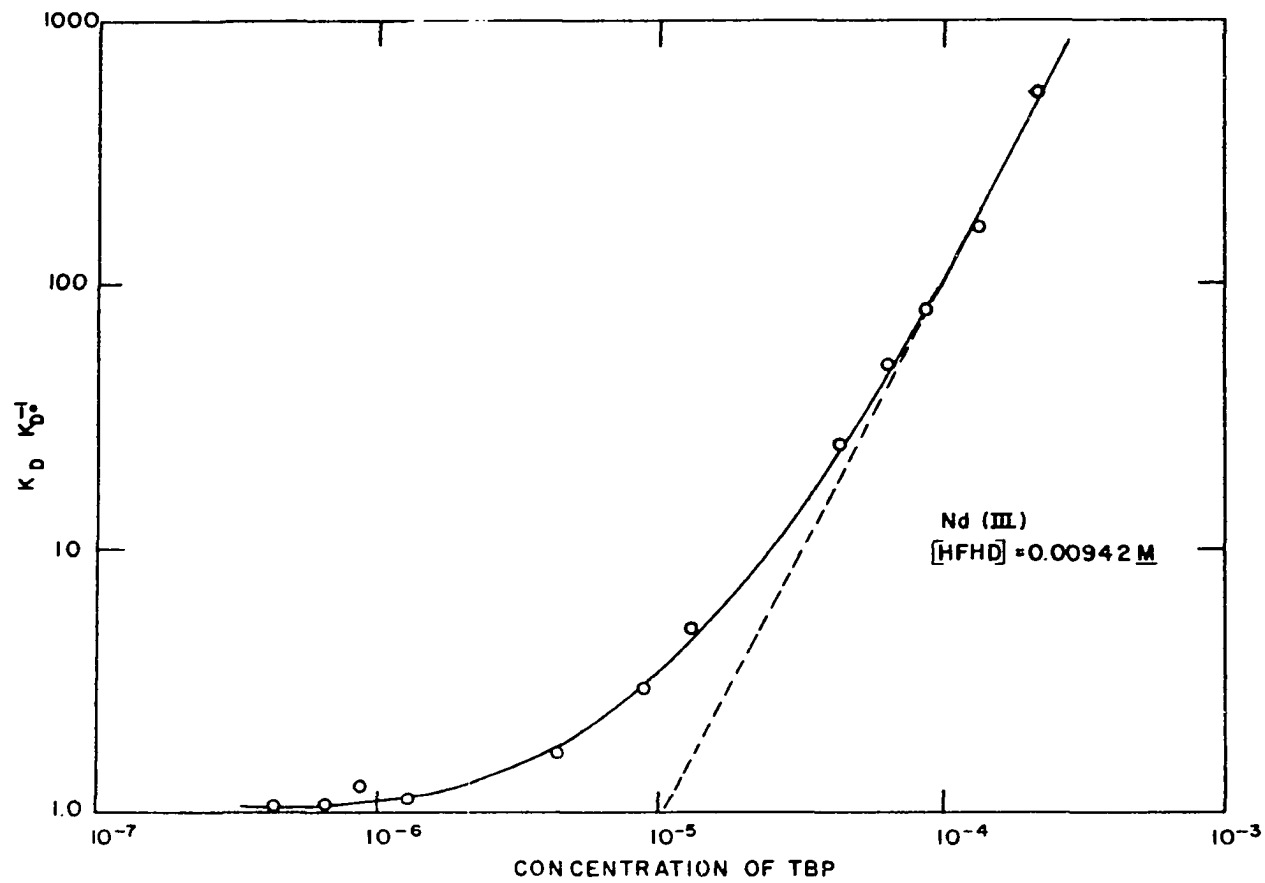


Figure 24. Dependence of the ratio, K_D / K_D^0 , on the concentration of TBP in the system, Nd(III)-HFHD-TBP-cyclohexane

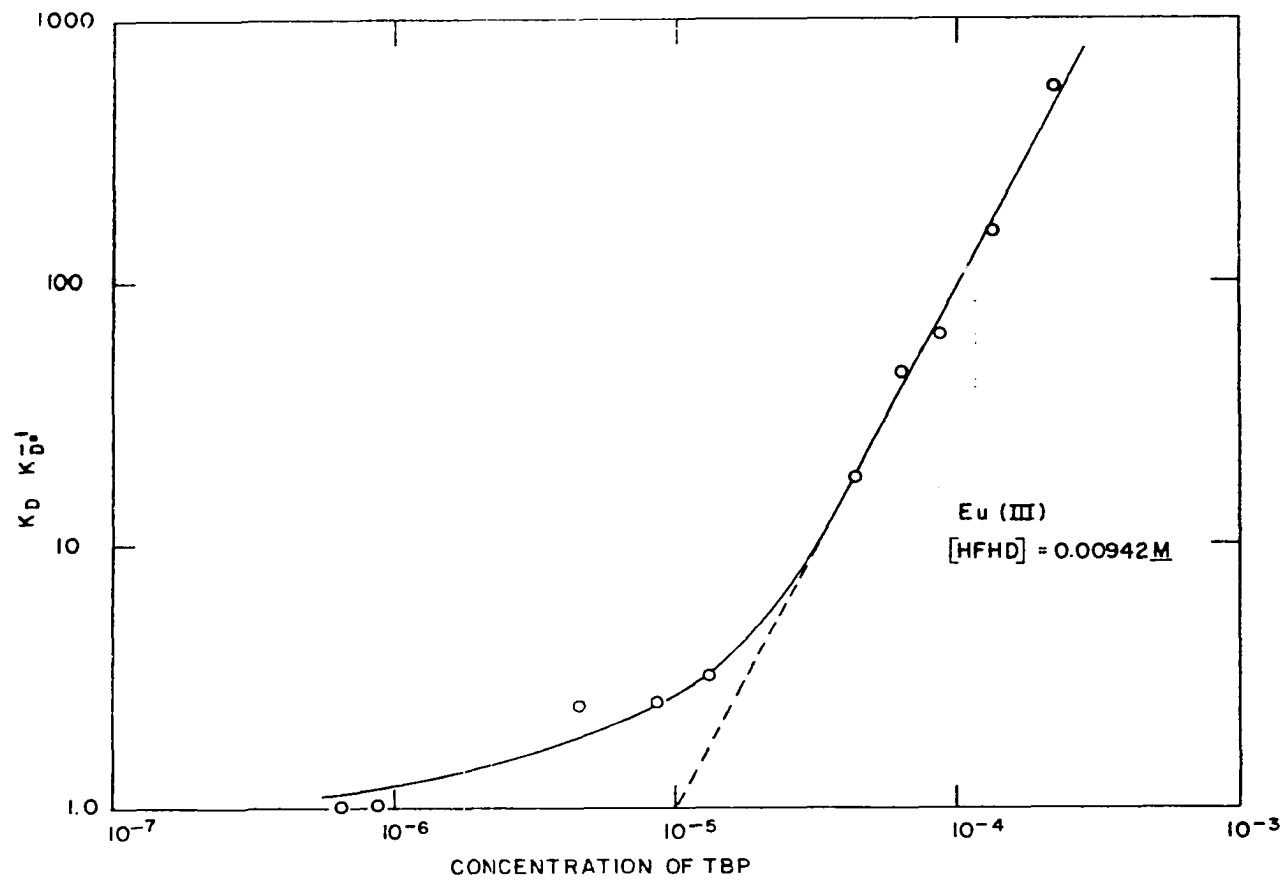


Figure 25. Dependence of the ratio, $K_D K_D^{-1}$, on the concentration of TBP in the system, Eu(III)-HFHD-TBP-cyclohexane

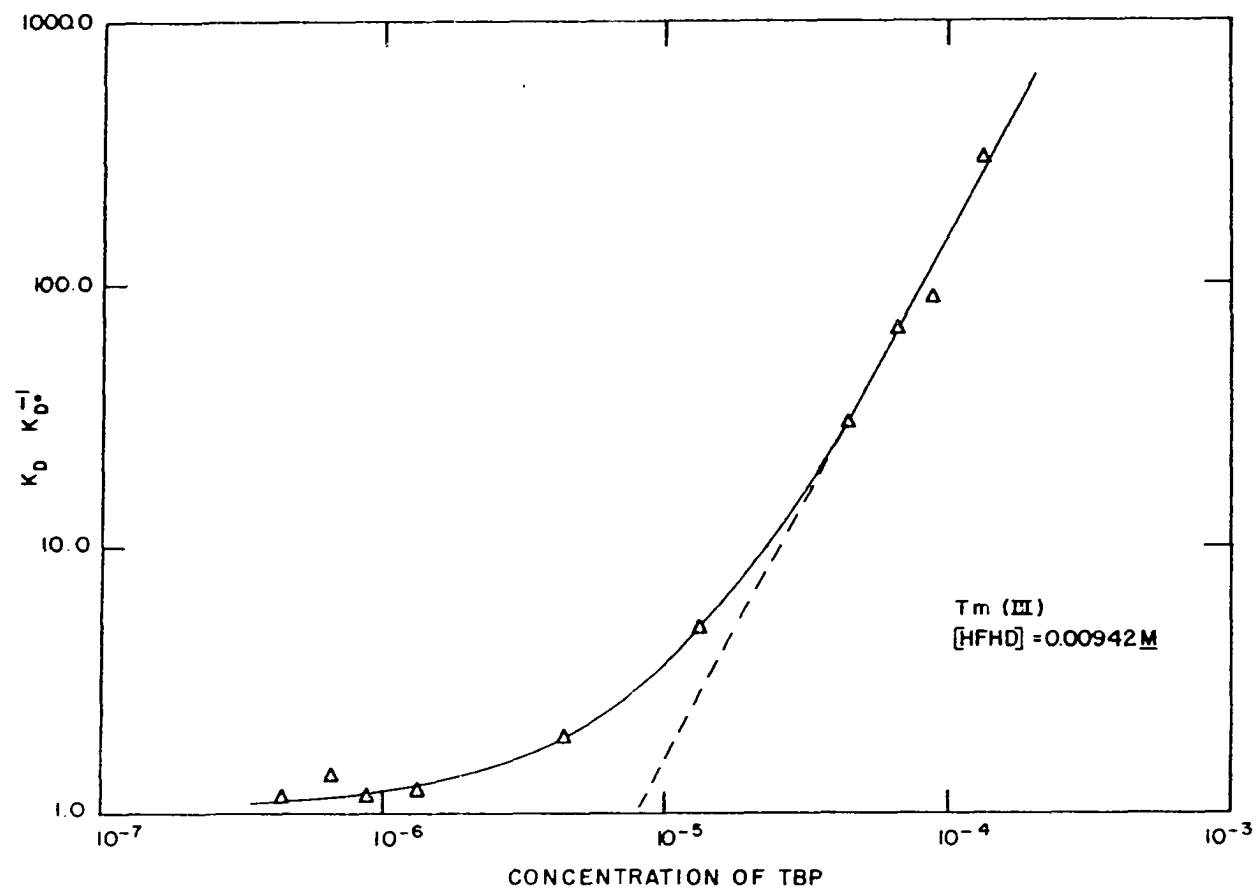


Figure 26. Dependence of the ratio, $K_D K_D^{-1}$ on the concentration of TBP in the system, Tm(III)-HFHD-TBP-cyclohexane

Several experiments were performed with HDODEFOD in order to determine the effect of chain length of the β -diketone on the composition of the chelate.¹⁵ The dependence of the extraction of Nd(III), Eu(III) and Tm(III) on the concentration of TBP in the presence of HDODEFOD is shown in Figure 27. The respective slopes, 1.9, 2.1 and 2.1, obtained from a least squares treatment of the experimental data, indicated the formation of the diadduct complexes. The measured distribution ratios for Tm(III) suggested that quantitative extraction of micro levels of rare earth may be achieved with low concentrations of this ligand.

Separation of Cations by Liquid-Liquid Extraction

Measurement of distribution curves

Several elements commonly occur along with rare earths in ores and alloys and as impurities in nuclear by-product materials. In order to determine the utility of systems used in this research for effecting practical separations by solvent extraction, distribution curves were measured for several elements. Aqueous solutions initially 10^{-4} M in the

¹⁵This ligand contained 3 to 5% of an impurity which was not removed by fractional distillation or by precipitation of the copper chelate.

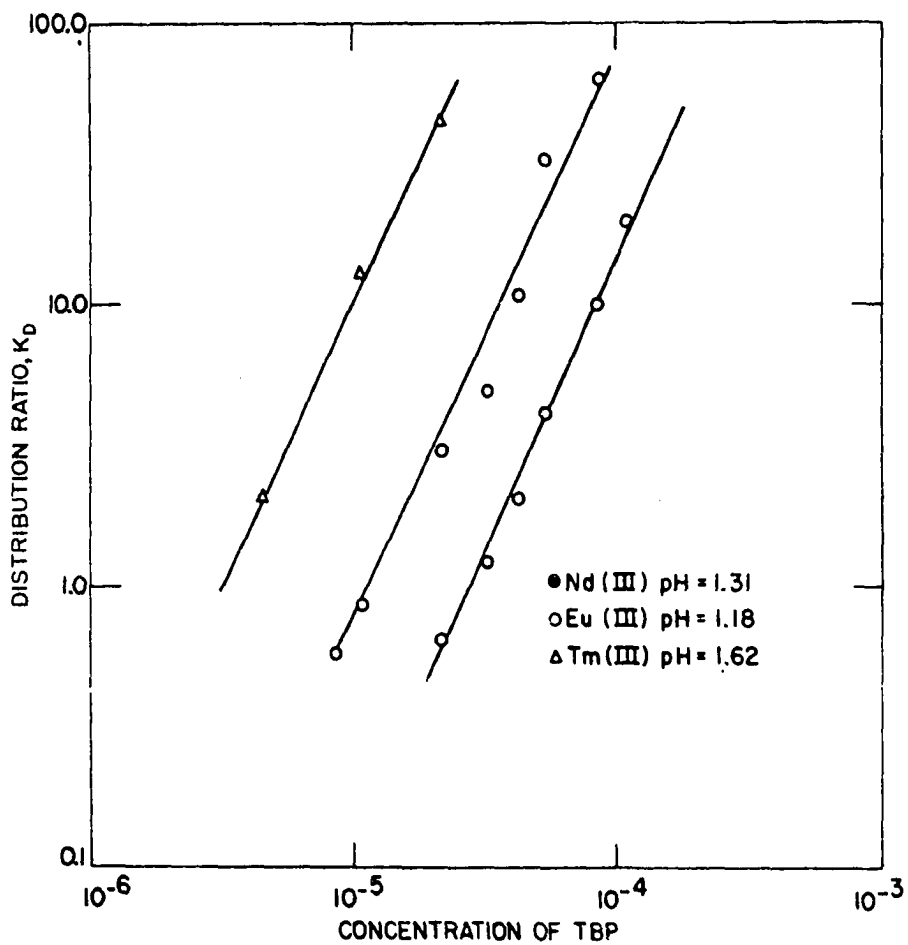


Figure 27. Dependence of the distribution ratio on the concentration of TBP in the system R.E.-
0.0172 M HDODEFOD-TBP-cyclohexane

cations were extracted with organic phases containing the same ligand concentrations employed in previous studies of the extraction of the lanthanides. Accurate predictions of the separation of cations should be possible since distribution curves were measured at high ligand to metal ratios. In these experiments the extraction systems were shaken overnight and analyzed the following morning. Preliminary experiments and information obtained from the literature showed that a 60-minute shaking period was usually sufficient for extraction equilibrium to be attained.

The limited extraction of rare earths into solutions of HTFA in benzene was previously shown in Figure 7. This behavior of the rare earths should allow the separation of several cations which commonly occur as impurities in the rare earths. The data available in the literature on the extraction of cations with HTFA were previously discussed during the LITERATURE REVIEW. This information and the data shown in Figure 8 may be used to select conditions for the separation of Al(III), Be(II), Zr(IV), Fe(III), Ga(III) and In(III) from each other and from the rare earths. Other important impurities or related elements include Th(IV), Ca(II), U(VI), Y(III) and Sc(III). Distribution curves for the extraction of Th(IV),

Sc(III), U(VI), and Tm(III) are shown in Figure 28. Corresponding data for the extraction of Lu(III) was previously plotted in Figure 7. These data indicate that scandium and thorium can be separated from all rare earths by a single extraction if the equilibrium pH is maintained in the range 3.0 to 3.5. The pH range can be increased according to the data shown in Figure 7 in the event that all rare earths are not present in the mixture containing thorium or scandium. The synergic extraction curves for the distribution of Th(IV), Sc(III), U(VI) and Eu(III) into solutions of HTFA-TBP in cyclohexane are shown in Figure 29. These curves indicated that thorium and U(VI) can be separated from the rare earths by carefully controlling the pH. The extraction of Th(IV), Pr(III), Eu(III), Sc(III) and U(VI) into solutions of HHFA and TBP in cyclohexane is shown in Figure 30. Thorium is the only element shown that can be effectively separated from the rare earths at controlled pH. The extraction curves for calcium are plotted in Figure 31 and indicate a useful separation of the rare earths from calcium by extraction with HHFA and TBP in cyclohexane at an equilibrium pH of 2.0. It is also observed that calcium is quantitatively extracted using mixtures of HHFA and TBP in cyclohexane at $\text{pH} \geq 4.5$. The

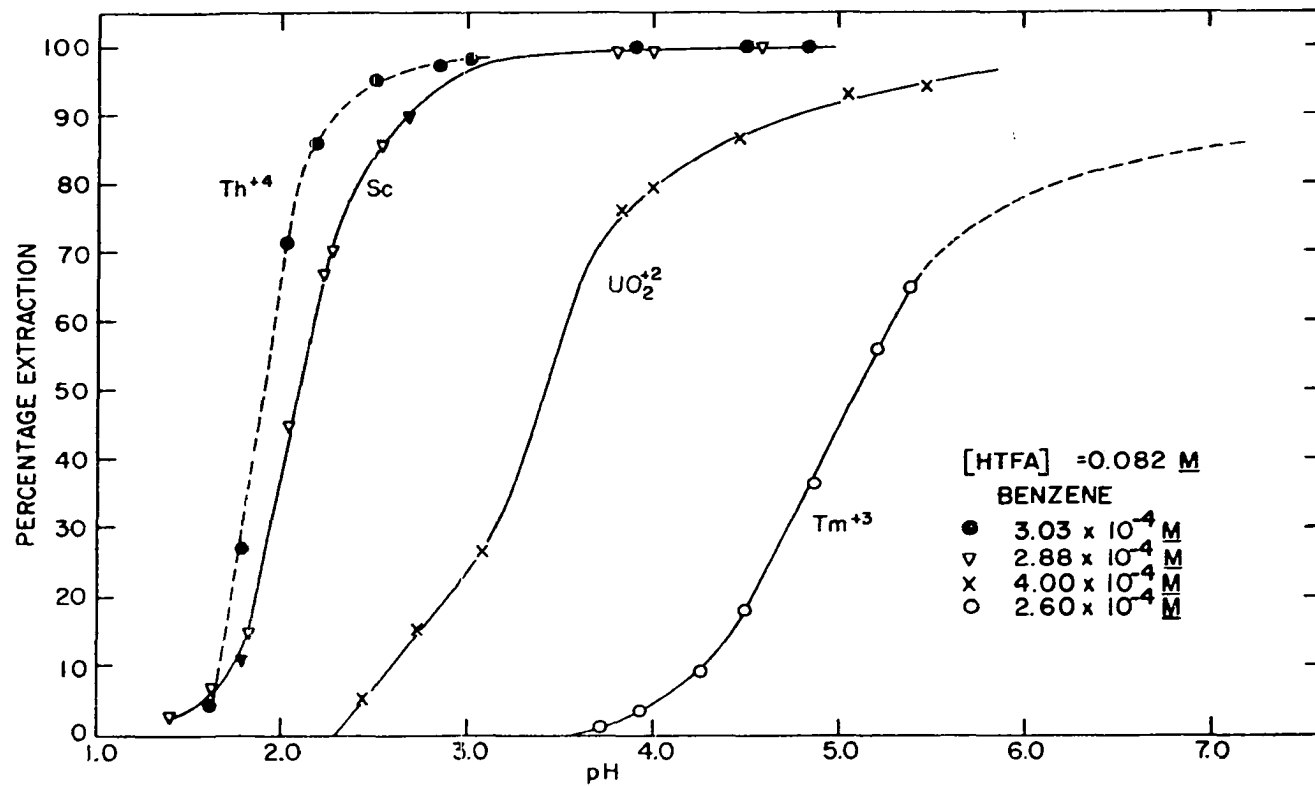


Figure 28. Extraction of cations with HTFA in benzene

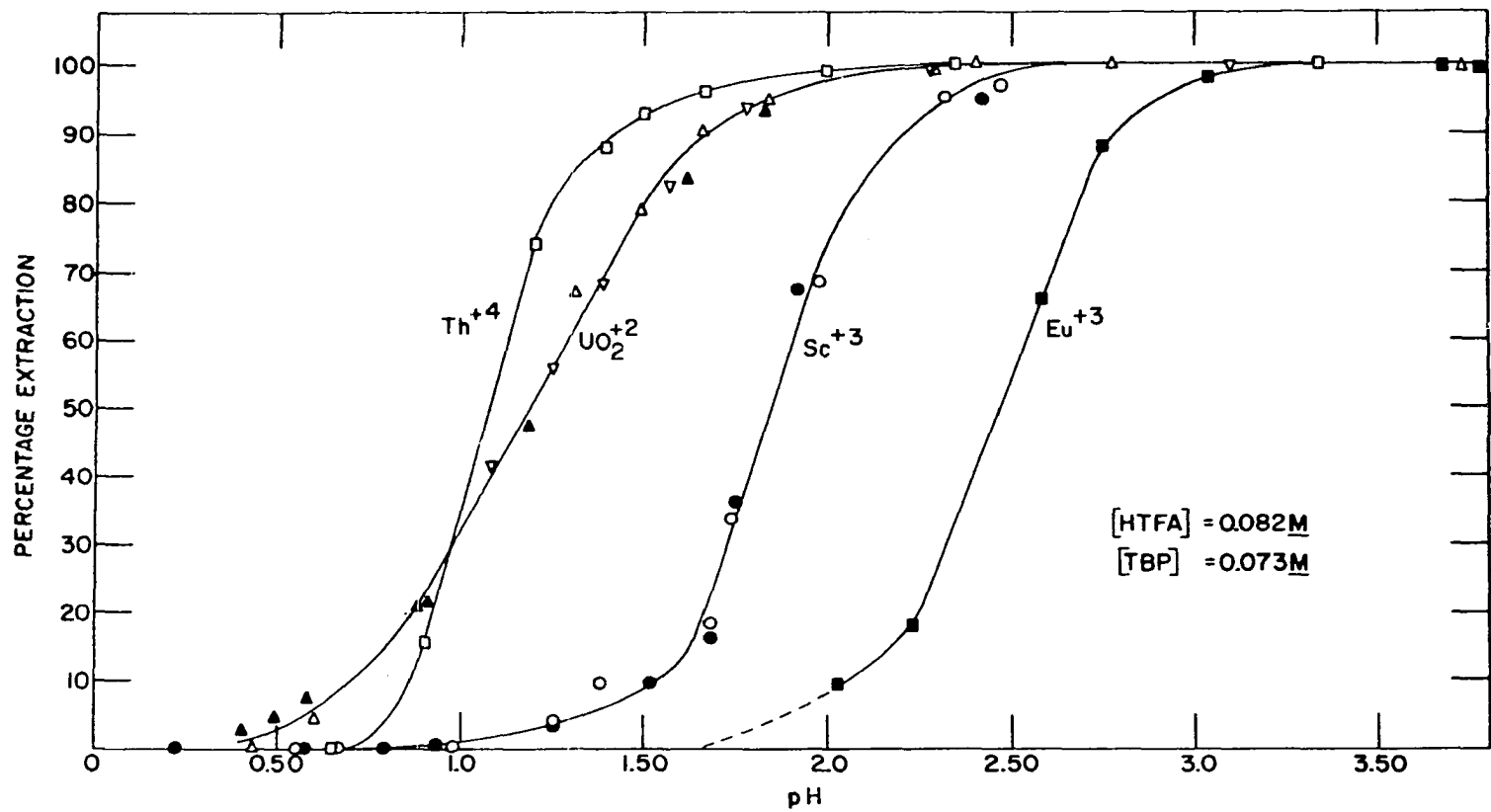


Figure 29. Extraction of cations with HTFA and TBP in cyclohexane

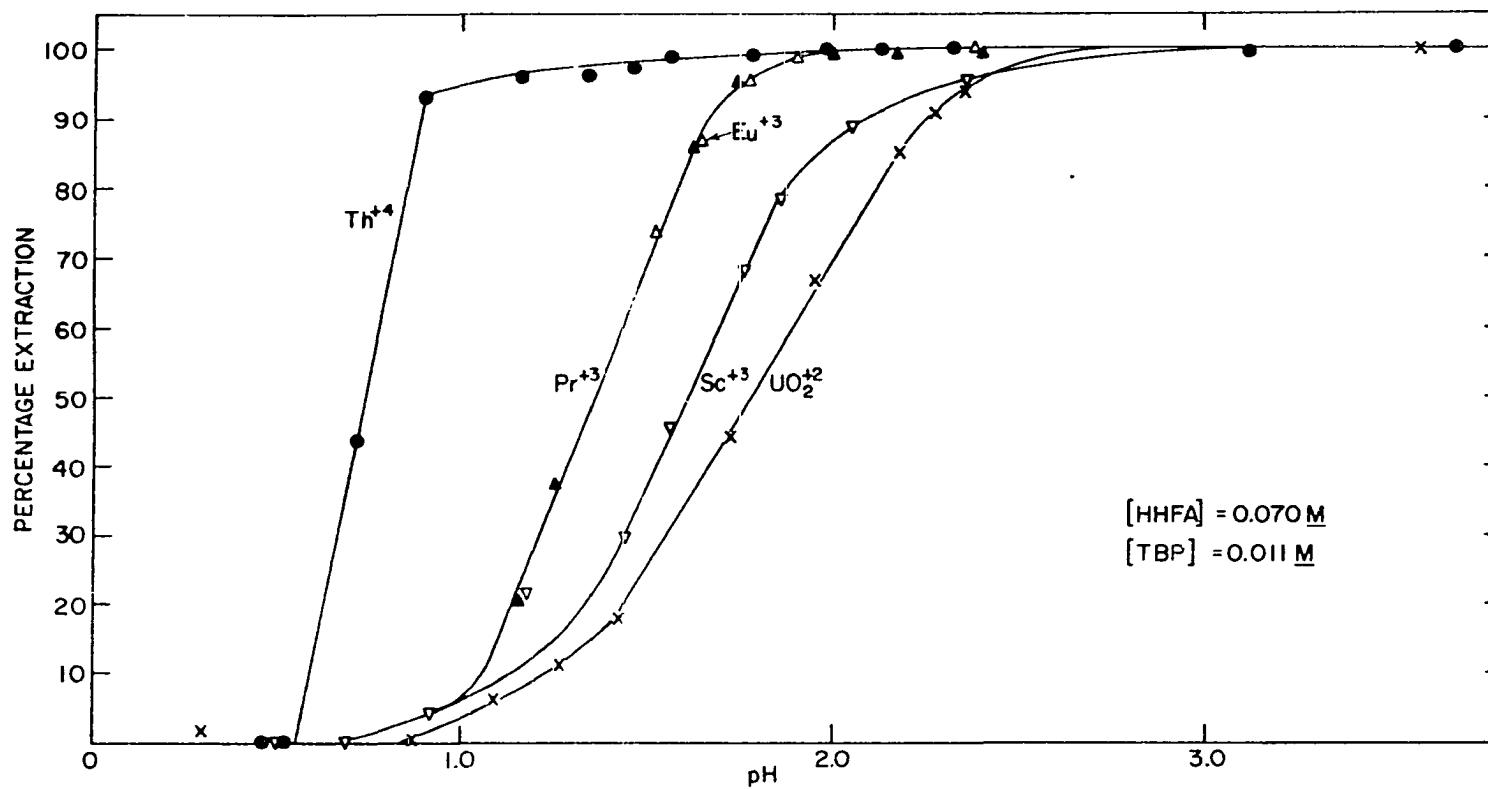


Figure 30. Extraction of cations with HHFA and TBP in cyclohexane

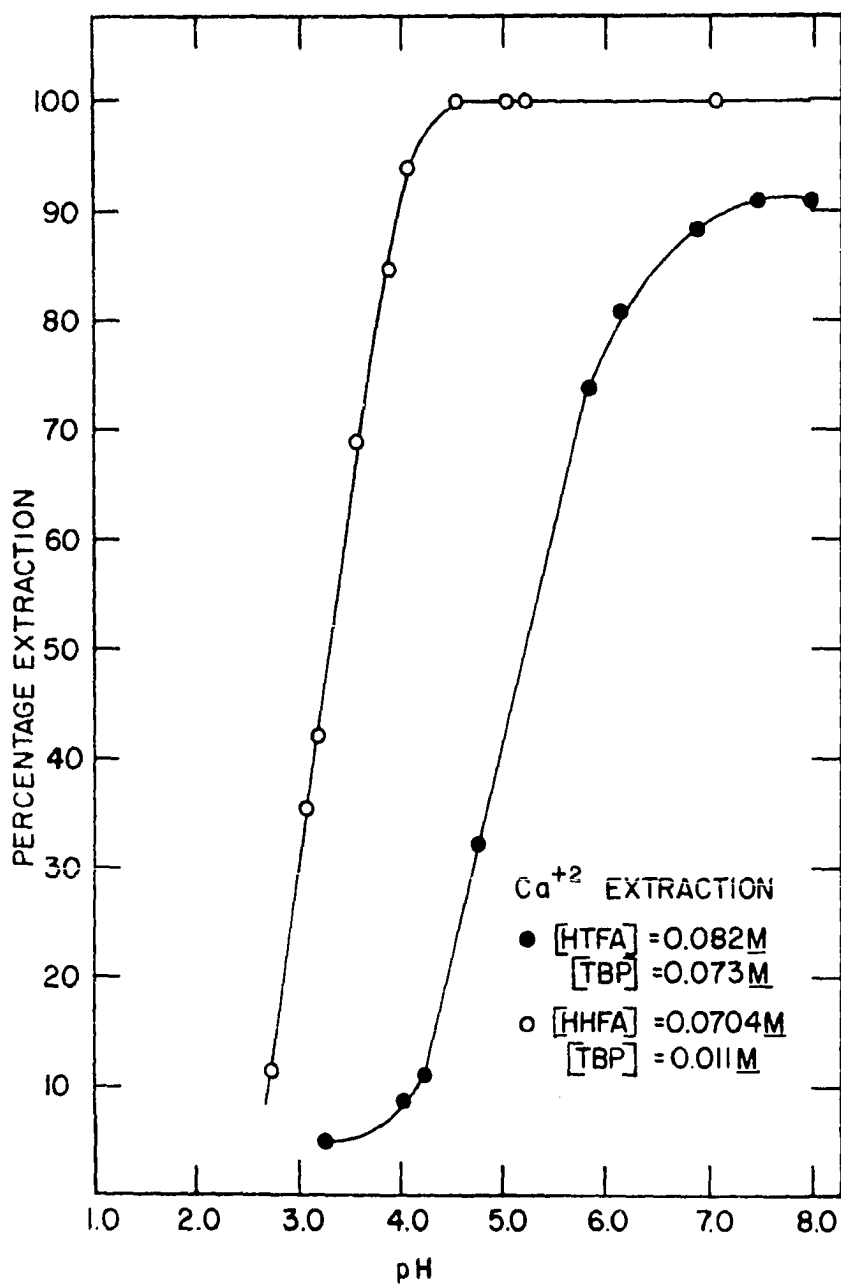


Figure 31. Synergic extraction of calcium with mixtures of HHFA and TBP and mixtures of HTFA and TBP in cyclohexane

extraction power of this system is significantly greater than that found by Sekine and Dyrssen for mixtures of HTTA and TBP. They reported that 90% extraction of calcium at pH 6.6 was accomplished by employing 0.1 M HTTA + 0.01 M TBP in CCl_4 . Distribution curves for Y(III) are plotted in Figure 32. It is seen that this element exhibits extraction behavior quite similar to that previously reported in this thesis for the rare earths. The distribution curves for the extraction of Cu(II) and Zn(II) with mixtures of HHFA and TBP and mixtures of HTFA and TBP in cyclohexane are shown in Figure 33. No useful separations of these elements from the rare earths can be achieved with the HHFA-TBP-cyclohexane system. Approximately 90% of the rare earth should be separated from Zn(II) by extraction with a mixture of HTFA and TBP in cyclohexane at pH 3.0.

Presumed stoichiometries of the species extracted into the organic phase are reported in Table 10 and are based on compositions reported in the literature for similar systems.

The relative positions of the extraction curves shown in Figures 28 to 33 are seen to be different for the two synergic systems. With the exception of the uranyl and Cu(II) cations the curves of the cations in the HTFA-TBP-cyclohexane system

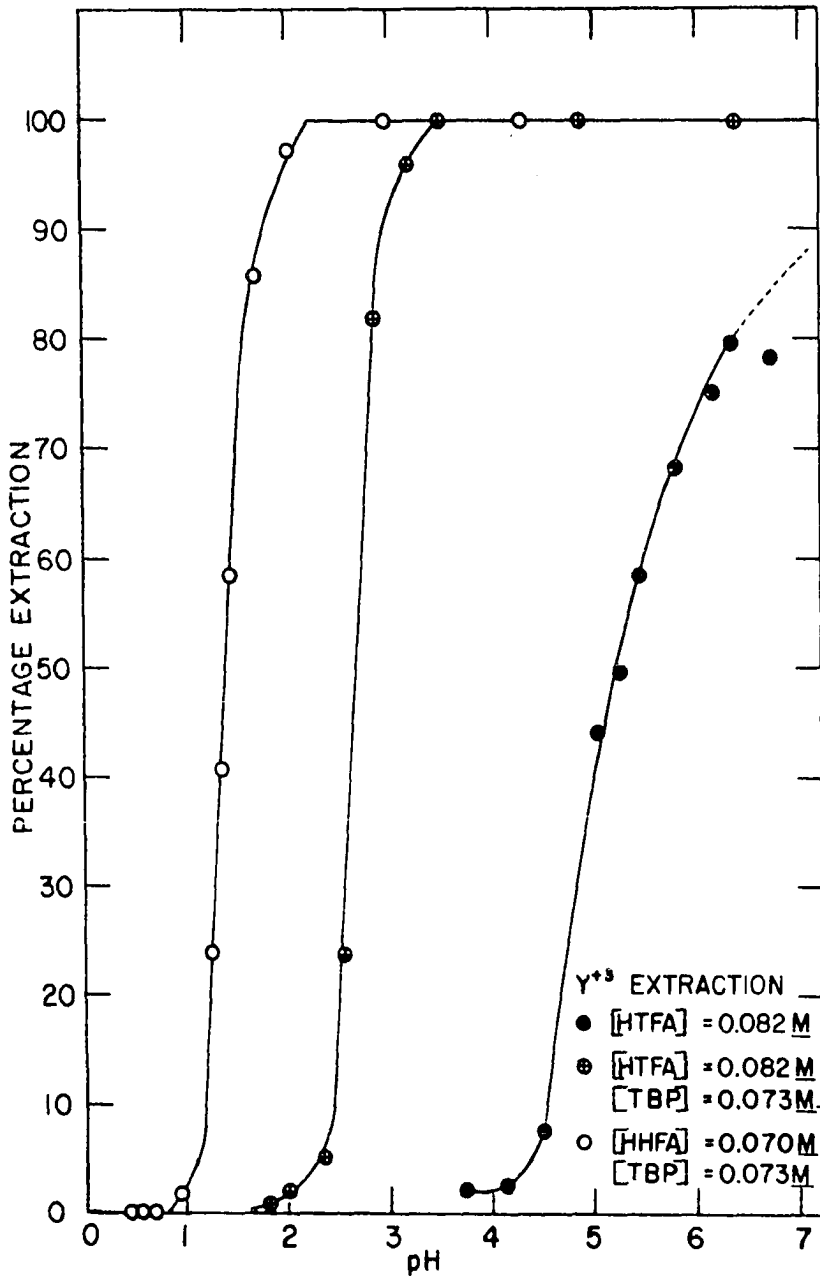


Figure 32. Distribution curves for the extraction of Y(III) with the HTFA-benzene system, the HTFA-TBP-cyclohexane and the HHFA-TBP-cyclohexane systems

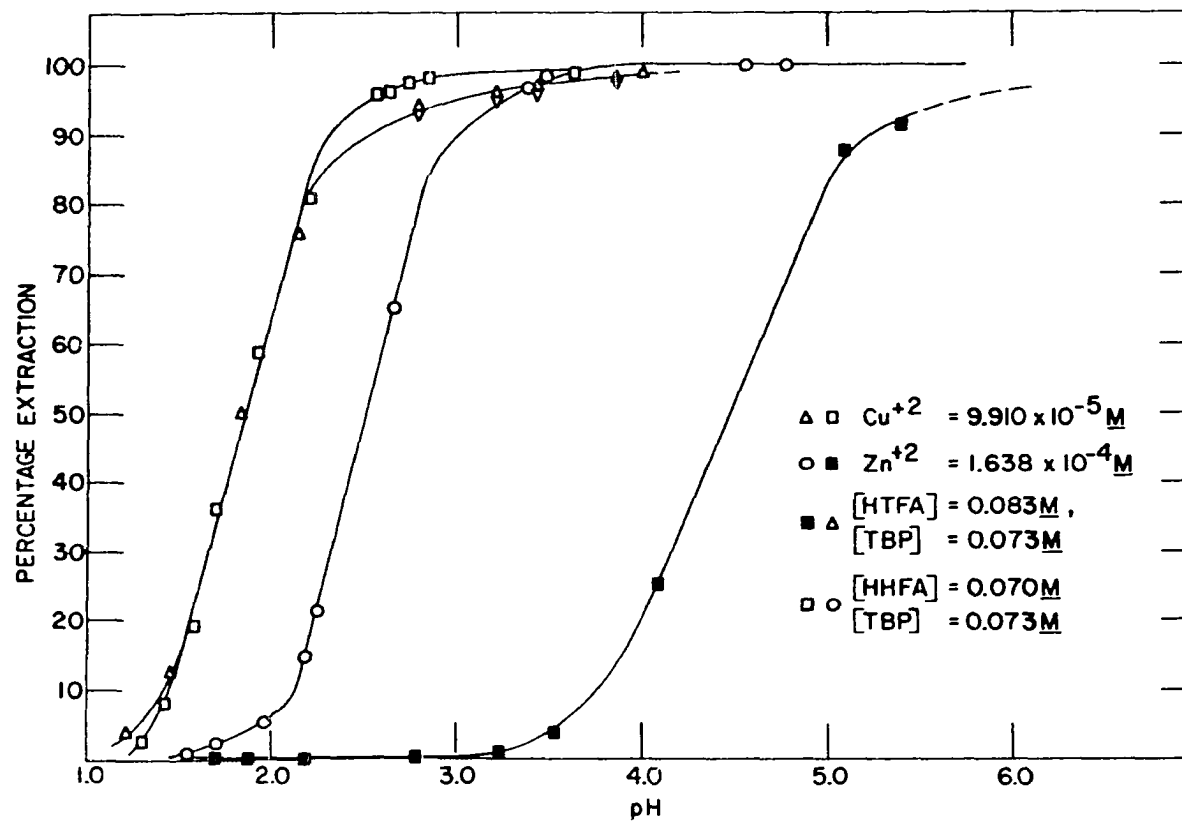


Figure 33. Synergic extraction of copper and zinc with mixtures of HHFA and TBP and mixtures of HTFA and TBP in cyclohexane

Table 10. Presumed stoichiometries of mixed-metal chelates

Presumed complex	Reported compositions	Reference
$\text{Th}(\text{A})_4\text{TBP}^{\text{a}}$	$\text{Th}(\text{TTA})_4\text{TBP}$	(47)
$\text{UO}_2(\text{A})_2\text{TBP}$	$\text{UO}_2(\text{TTA})_2\text{TBP}$	(59)
$\text{Sc}(\text{A})_3\text{TBP}$	$\text{Sc}(\text{TTA})_3\text{TBP}$	(106)
$\text{Y}(\text{A})_3(\text{TBP})_2$	R.E. $(\text{HFA})_3(\text{TBP})_2$	This thesis
$\text{Cu}(\text{A})_2\text{TBP}$	$\text{Cu}(\text{HFA})_2\text{TOPO}$	(71)
$\text{Zn}(\text{A})_2(\text{TBP})_2$	$\text{Zn}(\text{HFA})_2(\text{TOPO})_2$	(71)
$\text{Ca}(\text{A})_2(\text{TBP})_2$	$\text{Ca}(\text{TTA})_2(\text{TBP})_2$	(102)

^a A is the anion of HHFA or HTFA.

are positioned at higher pH values than those of the HHFA-TBP-cyclohexane system. The shift of the extraction curves to lower pH in the latter system is in agreement with a general rule which has been found useful in the prediction of the trends in the magnitude of the synergic effect (38). In view of the general inverse proportionality of the extent of synergic enhancement to the stability of the chelates of the β -diketones and because of the greater acidity of HHFA, the relative positions of the distribution curves of a given cation in the two systems are understandable, since HTFA usually forms stronger chelate complexes than HHFA.

The relative magnitude of the synergic effect for different cations can be conveniently compared by examining the differences in the $\text{pH}_{\frac{1}{2}}$ values in the normal and synergic system. If Eq. 16 is combined with the similar expression for the synergic system, the equation,

$$\Delta\text{pH}_{\frac{1}{2}} = \frac{1}{n} (\Delta \log K_{\text{eq}}) + \frac{m}{n} \log[D]_0^{16} \quad (33)$$

is obtained. The symbol, $\Delta\text{pH}_{\frac{1}{2}}$, is $\text{pH}_{\frac{1}{2}}(\text{normal}) - \text{pH}_{\frac{1}{2}}(\text{synergic})$ and the term, $\Delta \log K_{\text{eq}}$, corresponds to $\log K_{\text{eq}} - \log K_{\text{eq}}^{\text{O}}$. Equation 33 shows that the difference in pH at which 50% extraction occurs for the two systems is a direct measure of the change in stability of the chelate and mixed complexes. Values of $\Delta\text{pH}_{\frac{1}{2}}$ for several cations are shown in Table 11.

Table 11. Relative order of the synergic enhancement of cations by mixtures of HTFA and TBP in cyclohexane

Cation	$\text{pH}_{\frac{1}{2}}$ (HTFA)	$\text{pH}_{\frac{1}{2}}$ (HTFA+TBP)	$\Delta\text{pH}_{\frac{1}{2}}$
Eu^{+3}	6.50	2.47	4.03
Y^{+3}	5.20	2.60	2.60
UO_2^{+2}	3.38	1.19	2.19
Th^{+4}	1.90	1.07	0.83
Sc^{+3}	2.10	1.85	0.25

¹⁶ See APPENDIX for derivation.

The tabulated data show the largest synergic effect for the rare earth cation. A larger increase in solubility and stability which results from the ability to accommodate two adduct molecules seems to be a reasonable explanation for the greater synergic enhancement of the lanthanides. The other cations listed in Table 11 have been observed to form only monoadduct complexes. The relative order of enhancement found in this study is in agreement with stability constants determined by other investigators and reported by Newman (83).

The $\text{pH}_{\frac{1}{2}}$ values for the uranyl ion are shown in Table 12.

Table 12. $\text{pH}_{\frac{1}{2}}$ values for the extraction of uranium(VI) into cyclohexane

[HA]	[TBP] _o	$\text{pH}_{\frac{1}{2}}$
0.082 <u>M</u> HTFA	0.073 <u>M</u>	1.19
0.0704 <u>M</u> HHFA	0.073 <u>M</u>	1.57
0.0704 <u>M</u> HHFA	0.010 <u>M</u>	1.78

These results for U(VI) show a reversed trend from the order of the extraction of other cations in these two systems. Repeated measurements confirmed that UO_2^{+2} was extracted at a lower pH with cyclohexane solutions of HTFA and TBP than with solutions of HHFA and TBP in this solvent. This behavior is

contradictory to that predicted on the basis of the stabilities of the respective chelates of the β -diketones. Belford (10) reported that the infrared frequency of the carbonyl group increased in the order, $\text{UO}_2(\text{AA})_2 < \text{UO}_2(\text{TFA})_2 < \text{UO}_2(\text{HFA})_2$. This observation is indicative of a decrease in the stability of the chelates with an increase in the fluorination of the β -diketones. On the basis of the smaller stability of $\text{UO}_2(\text{HFA})_2$, it would be predicted that mixtures of HHFA and TBP would have a stronger synergic effect than mixtures of HTFA and TBP.

The observed behavior of the synergic extraction of U(VI) was examined by considering factors that affect the donor acceptance of the chelates of U(VI). The total electron density in the coordination sphere of the uranyl cation should consist of electron contributions from the uranium atom and electron occupancy of the molecular orbitals involved in π bonding to the oxygen atoms. Dyatkina (32) suggested that the linear uranium to oxygen bonds could be regarded as having a bond order of 3. McGlynn and Smith (75) combined appropriate atomic and molecular orbitals and described this bonding as consisting of one σ and two π bonds.

Evidence for nucleophilic effects of ligands equatorially

bonded to the UO_2^{+2} cation are available. Belford et al. (10) observed that the electronic transitions of the uranyl ion in the visible region were displaced toward higher frequencies in the series $\text{UO}_2(\text{AA})_2$, $\text{UO}_2(\text{TFA})_2$ and $\text{UO}_2(\text{HFA})_2$. Strong interactions of electrons in the uranyl bond with ligands in the equatorial plane were offered as an explanation for these spectral shifts (8). McGlynn and Smith (75) showed that the uranyl axial bond lengths increased with successive bonding to stronger ligands. They explained this weakening of the bond on the basis of ligand effects on the molecular orbitals of the uranyl ion through additional electron occupancy and increased electrostatic repulsion. The more basic anions of HTFA are more strongly attached to the uranyl cation than anions of HHFA (10). The greater basicity of the former is based on the reported pKa values of 6.3 for HTFA (118) and 4.6 for HHFA (118). This information indicates that ligand effects on electron contributions from the uranyl oxygens would be greater in the case of chelation to HTFA than those induced by complexation with HHFA. Greater ligand interactions for HTFA could result in a larger reduction in electron delocalization from the uranyl oxygens. The spatial distributions of electrons on the chelate molecule and the

relative contributions to the total electron density provided by the carbonyl oxygens of the β -diketones and the π bonded uranyl oxygens are not known. It is therefore not conclusive that a second order effect of a greater reduction in the uranyl oxygen contributions through bonding to anions of HTFA would result in a stronger Lewis acid chelate complex than that obtained by complexation with HHFA. However, it is evident from the quoted literature that ligand effects are operative. These factors are considered to be partly responsible for the observed extraction behavior.

Contributions from chemical factors that influence the distribution of the uranyl cation were also considered. The stability constants, β_n , for $(\text{UO}_2\text{Ac})^+$, 410; $\text{UO}(\text{Ac})_2$, 8×10^4 ; and $(\text{UO}_2(\text{Ac})_3)^-$, 2×10^6 ; were reported by Sary (117). Complexation by chloride is negligible in view of the stability constant of 0.88 for UO_2Cl^+ (27). The extraction of the uranyl cation from aqueous-NaCl-HCl phases at 0.50 ionic strength into solutions of HTFA and TBP and of HHFA and TBP in cyclohexane was studied to determine the effect of acetate ions. The $\text{pH}_{\frac{1}{2}}$ values obtained at concentrations of reagents identical to those given in the first two columns of Table 12 were 1.10 and 1.12, respectively, for $\text{UO}_2(\text{TFA})_2\text{TBP}$ and

$\text{UO}_2(\text{HFA})_2\text{TBP}$. The constancy of the position of the curves for the HTFA-TBP-cyclohexane system and the change in that of the HHFA-TBP system from 1.57 in the acetate-chloride medium is consistent with more competitive complexation in the aqueous phase by acetate in the presence of HHFA than that occurring in the presence of HTFA. The reaction, $\text{UO}_2^{+2} + 2\text{Ac}^- + \text{TBP}_{(o)} \rightleftharpoons \text{UO}_2\text{Ac}_2 \cdot \text{TBP}_{(o)}$ was shown to be insignificant. After the equilibration of aqueous phases containing UO_2^{+2} with 0.073 M solution of TBP in cyclohexane, no UO_2^{+2} species could be detected by spectrophotometric methods in the organic phase and analysis of the aqueous phases showed no decrease in the initial $[\text{UO}_2^{+2}]$. It is proposed that the cumulative action of the aforementioned factors is responsible for the observed extraction behavior of the uranyl ion in the systems studied. Other investigators have reported contradictions to the synergic effect that would be predicted on the basis of chelate stabilities. Ke and Li (66) obtained constants for the reaction of alkyl amines with $\text{Cu}(\text{TTA})_2$ which were larger than those observed for $\text{Cu}(\text{TFA})_2$ even though the latter is the stronger Lewis acid. They attributed this behavior to the fact that the bulky R_3N group could force the 2-thenoyl group out of the molecular plane thus destroying the resonance with

the chelate ring. They postulated that the resulting localization of the ring electron density increased the acidity of $\text{Cu}(\text{TFA})_2$ above that of $\text{Cu}(\text{TFA})_2$.

The extraction curves plotted in Figure 33 show a larger difference in the synergic effect between mixtures of HTFA and TBP in cyclohexane and mixtures of HHFA and TBP in this solvent for Zn(II) than for Cu(II). Dyrssen (33) reported that stability constants for adduct formation with TBP showed $\text{Zn}(\text{TFA})_2$ to be a better electron acceptor than $\text{Cu}(\text{TFA})_2$. The marked difference in the positions of the extraction curves for zinc is attributed to diadduct formation of $\text{Zn}(\text{HFA})_2$ while $\text{Zn}(\text{TFA})_2$, $\text{Cu}(\text{HFA})_2$ and $\text{Cu}(\text{TFA})_2$ formed monoadducts. The presumed composition of $\text{Zn}(\text{TFA})_2\text{TBP}$ was based on the reported complex $\text{Zn}(\text{TFA})_2\text{TBP}$ (33). The proximity of the $\text{Cu}(\text{HFA})_2\text{TBP}$ and $\text{Cu}(\text{TFA})_2\text{TBP}$ curves appears to corroborate the observations of Belford *et al.* (9). They noted that $\text{Cu}(\text{TFA})_2$ formed weakly stable monoadducts with ethanol while no complex could be isolated for $\text{Cu}(\text{HFA})_2$ which was expected to form a more stable monoadduct complex.

Quantitative separations

The extraction curves shown in this section and information available in the literature were used to choose conditions for practical separations of cations from the lanthan-

ides. Tracer techniques were used to determine the extent of separation of Sc(III) from Tm(III), Fe(III) from Eu(III) and Nd(III) from Al(III). The distribution of each element in the mixture was followed by performing duplicate experiments in which the respective tracers were employed. The extraction of aluminum was measured by atomic absorption spectroscopy. The efficiency of the separations was based on the recovery of the initial γ -activities and on the percentage of the extraction of the cations. The separations of U(VI) and Th(VI) from mixtures of Nd(III), Eu(III) and Tm(III) were studied by spectrophotometric and tracer techniques. The extraction of U(VI) and Th(IV) from aqueous phases initially containing only the respective elements was measured by spectrophotometric analysis of the aqueous phase after performing the required number of successive extractions with the organic phase. Arsenazo and Arsenazo III were used for the determination of these cations, respectively. Duplicate experiments in which the initial concentrations of uranium and thorium and the pH were identical to those used in the previously described extraction were performed in the presence of a mixture of the tracers of Nd(III), Eu(III) and Tm(III). The initial activity from the naturally radioactive uranium and thorium elements was less than 0.3% of the combined activity of the rare earth elements.

Corrections for this activity were applied in the calculation of the percentage extraction of the rare earths.

In order to obtain quantitative separations (~99% extraction of one element and <1% of the other) during a single extraction, it was necessary to control carefully the equilibrium pH in the appropriate region. The extent of separation achieved in some cases was found to be critically dependent on the equilibrium pH. Preliminary extraction experiments were conducted using sodium acetate-acetic acid buffers to ensure that the equilibrium pH of the aqueous phase was precisely controlled in the desired region.¹⁷

The ion pairs which were studied were chosen to illustrate the potentials of the different extraction systems for the separation of cations. Table 13 shows data for separations with 0.082 M solutions of HTFA in benzene. The data for scandium in the presence of Tm and the distribution curve for Lu shown in Figure 8 confirmed that scandium can be separated from all rare earths at pH 3.0 to 3.5 with approximately 2% of the initial scandium remaining in the aqueous phase. Fe(III) was quantitatively separated from europium at conditions for

¹⁷These results may prove to be useful for choosing appropriate buffers for pH control in other experiments and are reported in the APPENDIX.

Table 13. Separations of cations with 0.082 M solutions of HTFA in benzene

Separation ^a			% Extraction		% Recovery		Equilibrium pH	
Sc	from Tm	Tm	Sc	Tm	Sc	Tm	Sc	Tm
0.015 M		8.64x10 ⁻⁵ M	98.7	0.21	97.1	98.9	3.60	3.65
2.46x10 ⁻³ M		8.64x10 ⁻⁵ M	99.3	0.37	99.8	99.4	3.42	3.48
2.46x10 ⁻⁴ M		8.64x10 ⁻⁵ M	97.3	0.07	101.0	99.4	2.86	3.00
					99.3±1.5 ^b	99.2±.2 ^b		
Fe ⁺³	from	Eu ⁺³	Fe ⁺³	Eu ⁺³	Fe ⁺³	Eu ⁺³	Fe ⁺³	Eu ⁺³
1.00x10 ⁻² M		1.032x10 ⁻⁵ M	99.1	0.00	98.5	99.1	2.62	3.22
1.00x10 ⁻³ M		1.032x10 ⁻⁴ M	99.8	0.14	100.8	100.6	3.06	3.58
1.00x10 ⁻⁴ M		1.096x10 ⁻² M	99.8	0.04	100.3	100.9	3.08	3.38
<10 ⁻⁶ M ^c		≈10 ⁻⁸ M ^c	99.5	0.10	98.8	93.9 ^d	2.45	3.13
					99.9±0.9 ^b	100.2±0.7 ^b		

^aSeparation obtained by equilibration of aqueous phase with an equal volume of benzene.

^bAverage recovery values.

^cTracer elements only, other cation concentrations were provided by addition of known amounts of carrier.

^dValue omitted from calculation of mean.

which less than 0.2% of any rare earth would be extracted. Other elements which could be separated from rare earths with this reagent were previously mentioned.

Few investigators have attempted separations by synergic extraction since separation factors in these systems are usually smaller than those found in normal β -diketone extractions. However, when a common rare earth impurity element is coordinatively saturated by chelation with the β -diketone it will not form adduct complexes. In this case an improvement in the separation of the lanthanide should be obtained. The data in Table 14 show the utility of the synergic system, 0.0704 M HHFA-0.073 M TBP in cyclohexane, for the separation of neodymium from aluminum. All rare earths can be separated from aluminum under these conditions. Similar conditions should also allow the selective separation of rare earths from beryllium. Extraction curves shown in Figure 31 and the data in Table 5 indicate that rare earths in the presence of calcium can be selectively extracted with a mixture of HHFA and TBP in cyclohexane at pH 2.0.

The data in Table 15 show that multiple extractions with solutions 0.082 M in HTFA and 0.073 M TBP in cyclohexane produced quantitative separations of U(VI) and Th(IV) from mixtures of Nd, Eu and Tm. These data demonstrate that aqueous

Table 14. Separation of Nd(III) from Al(III) with cyclohexane which was 0.0704 M in HHFA and 0.073 M in TBP

Separation ^a			% Extraction		% Recovery		Equilibrium pH	
Nd	from	Al	Nd	Al	Nd	Al ^b	Nd	Al
1.217x10 ⁻² <u>M</u>		1.180x10 ⁻² <u>M</u>	99.9	--	99.6	100.5	3.01	3.03
1.217x10 ⁻³ <u>M</u>		1.180x10 ⁻² <u>M</u>	100.0		98.8	98.6	2.65	2.55
1.217x10 ⁻⁵ <u>M</u>		1.180x10 ⁻² <u>M</u>	99.8		99.8	99.2	3.10	3.15
					99.4±0.4 ^c	99.4±0.7 ^c		

^aOne step extraction with equal aliquots of aqueous and organic phases.

^bThe recoveries of Al were calculated by comparing the concentration of aluminum found in the aqueous phase by analysis after extraction to the original concentration in the aqueous phase before extraction.

^cAverage recovery values.

Table 15. Separation of U(VI) and Th(IV) from mixtures of the rare earths by extraction with cyclohexane which was 0.082 M in HTFA and 0.073 M in TBP

UO_2^{+2} from R.E. ^a		% of UO_2^{+2} remaining in aqueous phase	Rare earth % E % R		Number of extractions	Equilibrium pH
0.050 <u>M</u>	4.0x10 ⁻⁵ <u>M</u>	0.18	0.25	100.0	7	1.05
			0.32	99.9	9	1.13
Th(IV) from R.E.		% Th(IV) remaining in aqueous phase	Rare earth % E % R		Number of extractions	Equilibrium pH
1.210x10 ⁻³ <u>M</u>	4.0x10 ⁻⁵ <u>M</u>	0.05	0.46	98.4	5	1.20
			0.23	99.5	6	1.10

^aR.E. is a mixture of the tracers of Nd, Eu and Tm.

solutions containing small amounts of rare earth in the presence of a large excess amount of UO_2^{+2} ($[\text{UO}_2^{+2}] \leq 1.25 \times 10^3$ [R.E.]) or Th impurities ($[\text{Th(IV)}] \leq 3.25 \times 10^2$ [R.E.]) were decontaminated by successive synergic extractions with mixtures of HTFA and TBP in cyclohexane. As much as 99.8% of the original UO_2^{+2} and 99.9% of the original Th(IV) were removed from the aqueous phase by manual shaking for one minute with fresh aliquots of cyclohexane containing the organic extractants. Less than 0.5% of the amount of the rare earths originally present was extracted. The maximum initial concentration of Th(IV) was restricted to 10^{-3} M because of precipitate formation for concentrations above this level. Precipitation did not occur in the case of the uranyl ion.

The results of these studies show that HTFA possessed greater capabilities than HHFA for the separation of impurities from the rare earths. Several elements were separated by HTFA in benzene and other possible separations were inferred. Quantitative separations were also achieved with the synergic system, HTFA-TBP-cyclohexane. It is evident that a selective extraction of rare earths is possible by first removing impurity elements during an extraction with HTFA in benzene and subsequently extracting the rare earth elements into mix-

tures of HTFA-TBP or HHFA-TBP in cyclohexane.

Experiments were performed to determine the effect of anions of HTFA on the gas chromatography of R.E.(HFA)₃(TBP)₂ complexes. Duplicate samples of 0.01 M solutions of each of the cations, La, Nd, Eu, Ho and Tm were prepared. One set of these solutions was selected as the standard samples and was buffered with sodium acetate-acetic acid mixtures at pH 4.00. The standard solutions were equilibrated for 30 minutes with an equal volume of cyclohexane which was 0.0704 M in HHFA and 0.073 M in TBP. The second set of solutions was extracted with benzene which was 0.082 M in HTFA. The organic phases of the latter were discarded after a back-extraction with 4.0 M HCl to recover any extracted rare earth. Aliquots of the aqueous phases of the sample solutions were acidified with concentrated HCl and evaporated to dryness. The rare earth residues were dissolved in a small volume of deionized water, buffered at pH 4.0 with a mixture of NaAc and HAc, and diluted to their original volume. Aliquots of the resulting solutions were extracted with an equal volume of cyclohexane which was 0.0704 M in HHFA and 0.073 M in TBP. The effectiveness of the experimental procedure for removing interferences from anions of HTFA during a subsequent extraction of rare earths with

HHFA and TBP dissolved in cyclohexane was determined by gas chromatography. The gas chromatograms of the organic phases from the set of standard solutions were compared with those obtained from the combined HTFA-benzene and HHFA-TBP cyclohexane extractions. The similar chromatograms of the complexes in the two sets of solutions indicated that no interferences from anions of HTFA occurred. Well defined peaks occurred for the R.E. above Eu and peak shapes for La and Nd were similar to those obtained by Butts (19).

Synergic Extraction of Uranium(IV) from Hydrochloric Acid

The distribution of U(IV) from aqueous phases initially 3.04×10^{-4} M in uranium into benzene which was 0.082 M in HTFA was measured as a function of pH and the extraction data are recorded in Table 16.

Table 16. Extraction of U(VI) into benzene which was 0.082 M in HTFA

pH	K_D	% E
1.33	2.374	70.4
1.54	3.261	76.5
1.73	3.584	78.0
2.09	2.212	68.9
2.26	0.525	34.4
2.54	0.587	37.0
3.93	7.911	88.8
4.27	9.992	90.0

The maximum extraction at pH 1.73 followed by decreasing distribution ratios to a minimum at pH 2.26 is representative of the known increase in oxidation and hydrolysis of U(IV) in weakly acidic solutions (13). At pH 2.40 the oxidized species, UO_2^{+2} , is extracted thereby producing a second region of increasing distribution into the organic phases.

The extraction of U(IV) into mixtures of HTFA-TBP and HHFA-TBP in cyclohexane was measured as a function of the concentration of HCl in the aqueous phase. The distribution curves plotted in Figure 34 show interesting extraction behavior in the two synergic systems. The rapid decrease in the extraction of U(IV) by mixtures of HTFA and TBP in cyclohexane could be expected at $[HCl]$ above 1.0 M in view of the acid dissociation constant of HTFA, 5.02×10^{-7} (118). Several factors were examined in order to explain the nature of the essentially acid independent extraction of U(IV) by mixtures of HHFA and TBP in cyclohexane. The extraction of chloride containing species of U(IV) was not likely to be responsible for the extraction behavior in the HHFA-TBP system since these complexes would also have been extracted in the HTFA-TBP system. In order to support this contention with experimental data, solutions of HCl which were also 0.00112 M in U(IV) were extracted with cyclohexane and with cyclohexane solutions

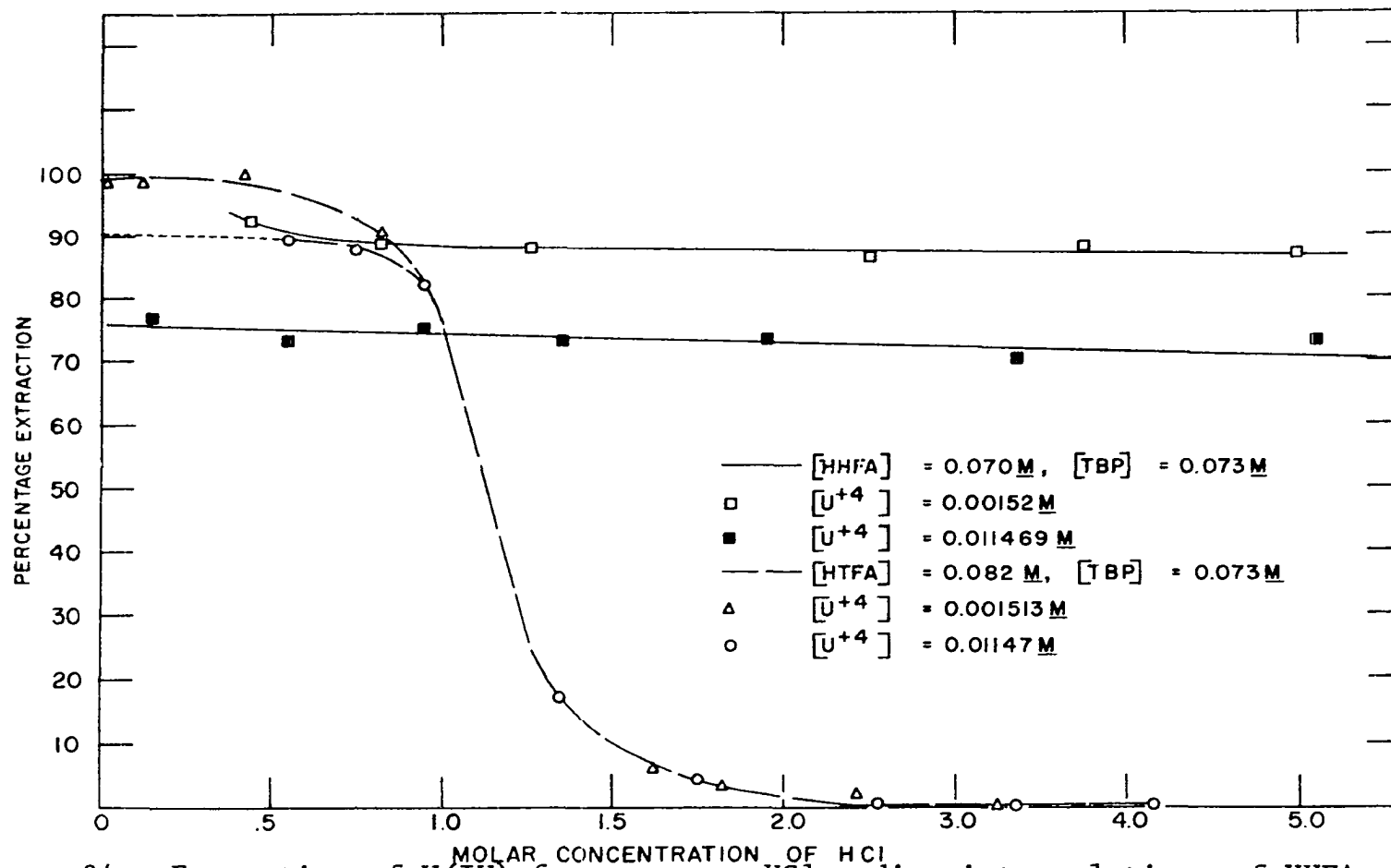


Figure 34. Extraction of U(IV) from aqueous HCl medium into solutions of HHFA-TBP and HTFA-TBP in cyclohexane

which were 0.073 M in TBP. No species of U(IV) were spectrophotometrically detected in the respective organic phases, and no loss of U(IV) from the aqueous phases was detected by spectrophotometric analysis with arsenazo. The reactions, $U(IV) + 4Cl^- \rightleftharpoons UCl_{4,(o)}$ and $U(IV) + 4Cl^- + xTBP_{(o)} \rightleftharpoons UCl_4TBP_x_{(o)}$ were therefore not important.

The absorption spectra of the U(IV)-complex extracted into cyclohexane solutions of HHFA and TBP was found to be identical to that obtained from solutions prepared by dissolving solid $U(HFA)_4$ in cyclohexane which was 0.0704 M in HHFA and 0.073 M in TBP. The absorbance of the adduct complexes of U(IV) is shown in Figure 35. In view of the adherence to Beer's Law at concentrations greater than those employed in solvent extraction, it is not likely that polymerization of the U(IV)-species in the organic phase was responsible for the observed extraction behavior in the HHFA-TBP system.

Evidence for the presence of sufficient anion concentration of HHFA for chelate formation in strongly acidic solution was obtained. A series of solutions which were 1.513×10^{-3} M in U(IV) and which were also 1.0 to 6.03 M in HCl were prepared. After a one-minute equilibration of these solutions with an equal volume of 0.0704 M solution of HHFA in cyclo-

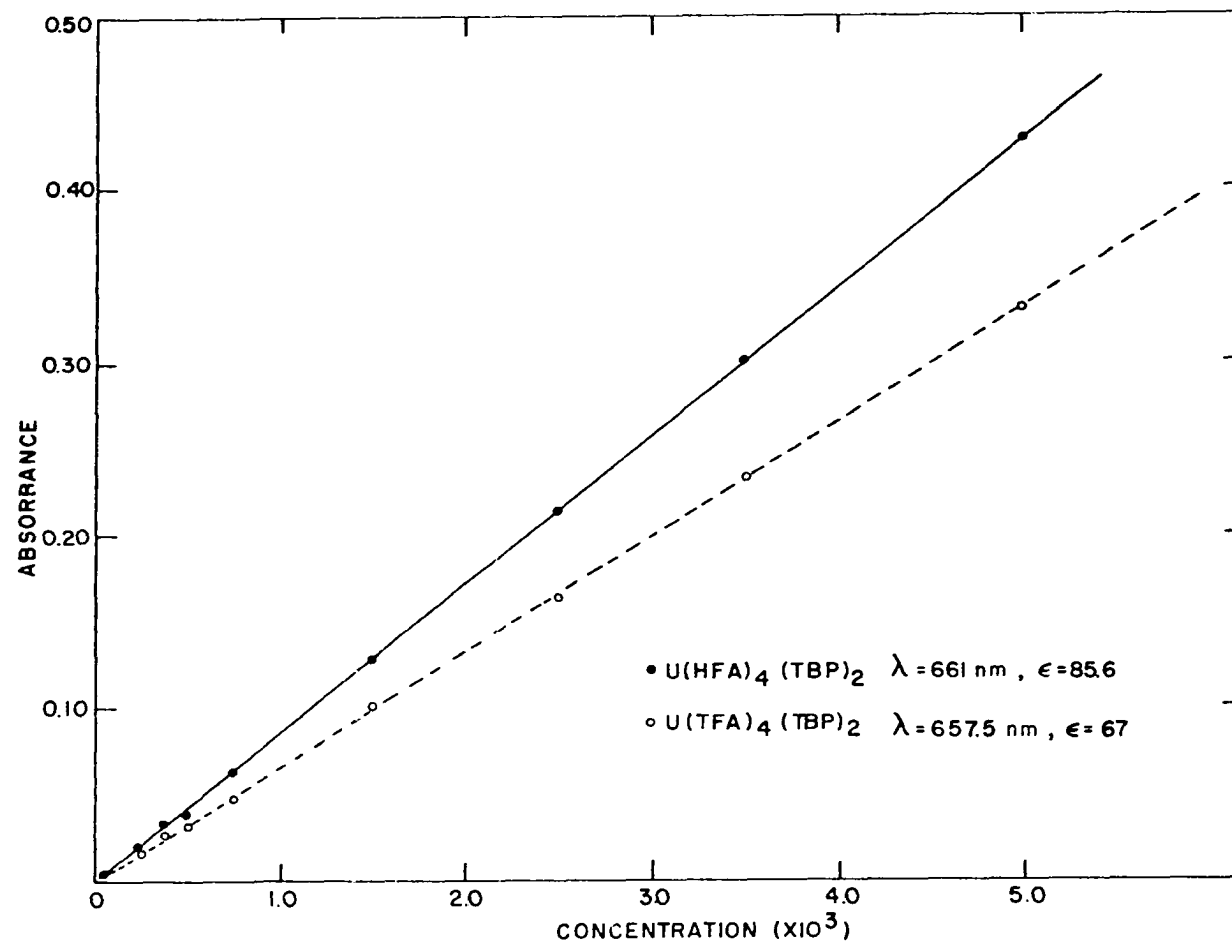


Figure 35. Absorbance of the adduct complexes of U(IV) as a function of the concentration of the chelates in cyclohexane

hexane, a specie containing uranium was extracted into the organic phase. The intense yellow-brown color of the organic phase was characteristic of those obtained during similar extractions of U(IV) with HTFA-TBP or HHFA-TBP in cyclohexane. The organic phases obtained during extraction with HHFA alone reverted to colorless after thirty minutes of shaking. Extraction of U(IV) from an aqueous phase $\geq 2.0 \text{ M}$ in HCl with HTFA in cyclohexane showed no evidence for the formation of a metastable uranium specie. After the extraction of U(IV) from 4.0 M HCl with 0.0704 M HHFA in cyclohexane, the absorption spectrum of the U(IV)-chelate of HHFA was measured and compared to the spectrum of the organic phase obtained by extraction of U(IV) into cyclohexane solutions of HHFA and TBP. The spectrum of a solution that was obtained by the dissolution of solid U(HFA)_4 in cyclohexane was also measured. These spectra are shown in Figure 36. A comparison of the spectra of the metastable intermediate and that obtained from the dissolution of solid U(HFA)_4 indicates that the anion concentration of HHFA in aqueous phases $\geq 2.0 \text{ M}$ in HCl is sufficient for substantial formation of U(HFA)_4 .

Although the nature of the metastability of the U(HFA)_4 complex was not studied by detailed mechanistic investigations

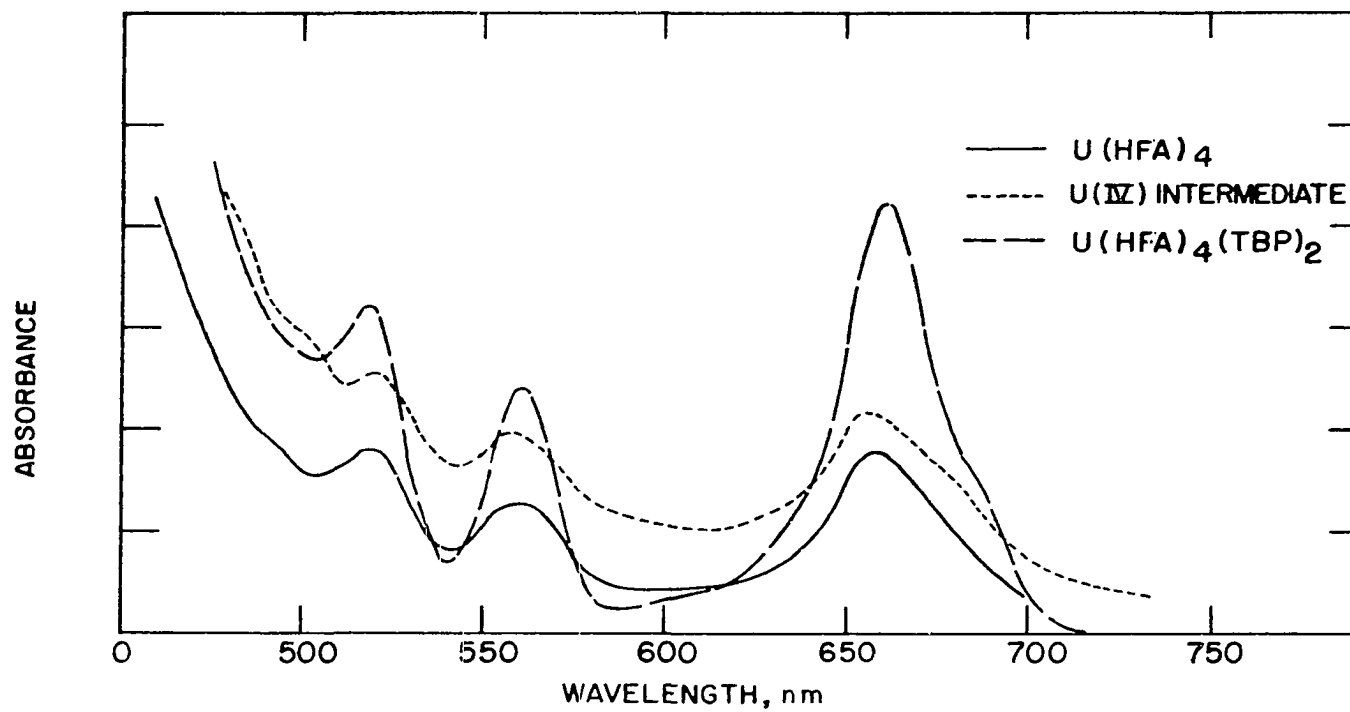


Figure 36. Absorption spectra of uranium(IV)-chelates in cyclohexane

during this research, several experimental observations offered pertinent information regarding factors affecting the extraction of U(IV) by mixtures of HHFA and TBP in cyclohexane. It was found that the metastable U(IV)-complex was rapidly formed and transferred to the organic phase. In the presence of TBP, a stable adduct complex was formed in the organic phase. The instability of the intermediate complex, $U(HFA)_4$, probably resulted from the reaction, $U(HFA)_{4,(o)} + 4HCl \rightleftharpoons UCl_4 + 4HHFA$. The destruction of the $U(HFA)_4$ complex through this reaction was shown by equilibrating a saturated cyclohexane solution of $U(HFA)_4$ with 3.0 \underline{M} HCl. The characteristic color of the organic phase disappeared after vigorous equilibration and no uranium chelate could be detected spectrophotometrically in the organic phase. Since the chelation reaction of U(IV) with HHFA and the subsequent transfer of the $U(HFA)_4$ complex to the organic phase proceeded faster than the destruction of the chelate by the above reaction, the rapid accumulation and subsequent disappearance of the chelate from the organic phase could result. The formation of a stable chelate of U(IV) in the synergic systems showed that adduct formation with TBP occurred in the organic phase. The reaction, $U(HFA)_{4,(o)} + nTBP_{(o)} \rightleftharpoons U(HFA)_4(TBP)_n_{(o)}$, formed a more

stable and soluble uranium complex than the reaction, $U^{+4} + 4HHFA \rightleftharpoons U(HFA)_4, (o)$. The increased solubility of the mixed complex was reflected by the fact that the amount of solid $U(HFA)_4$ dissolved in cyclohexane containing 0.0704 M HHFA + 0.073 M TBP was greater than that dissolved in pure cyclohexane.

The observed difference in the extraction behavior of U(IV) with HTFA-TBP and HHFA-TBP appears to be related to the greater acidity of HHFA and to the stronger tendency for adduct formation with chelates of HHFA (38,71). Other investigators have extracted large percentages of tetravalent cations from 4.0 M $HClO_4$ with 0.5 M thenoyltrifluoroacetone in benzene (55). It is therefore not unusual that the more acidic β -diketone, HHFA, in the presence of TBP would extract substantial quantities of U(IV) from acidic media.

The extraction of 1.513×10^{-3} M U(IV) by mixtures of 0.0942 M 1,1,1,5,5,6,6,7,7,7-decafluoro-2,4-heptanedione (HFDH) and 0.073 M TBP in cyclohexane is shown in Table 17. The large percentage of extraction of U(IV) indicates that the reduction of UO_2^{+2} and subsequent synergic extraction from 3 to 6 M HCl with a highly acidic β -diketone and TBP in cyclohexane would allow an easy separation of uranium from the

lanthanide elements.

Table 17. Extraction of U(IV) from HCl with HFHD and TBP in cyclohexane

HCl	K_D	E
1.00 <u>M</u>	101.99	99.0
2.93	30.11	96.8
3.90	15.59	94.0
4.87	23.44	95.9
6.03	12.86	92.8

TBP mole ratio studies on the U(IV)-HTFA-TBP-cyclohexane system

The results obtained from experiments to determine the number of TBP molecules bonded to $U(TFA)_4$ are reported in Figure 37. The formation of the monoadduct complex and its conversion to the diadduct are shown by these absorbance data. The composition of the extracted uranium chelates corresponded to $U(TFA)_4(TBP)_2$ and $U(HFA)_4(TBP)_2$. Few investigators have given evidence for 10-coordinated chelate complexes. A well-defined $M(\text{tropolonate})_5^-$ anion was prepared for Th(IV) and U(IV) (82). Mole ratio studies of other tetravalent actinide elements would probably confirm Muetterties' (82) prediction that coordination numbers of 10 should be relatively common for these elements.

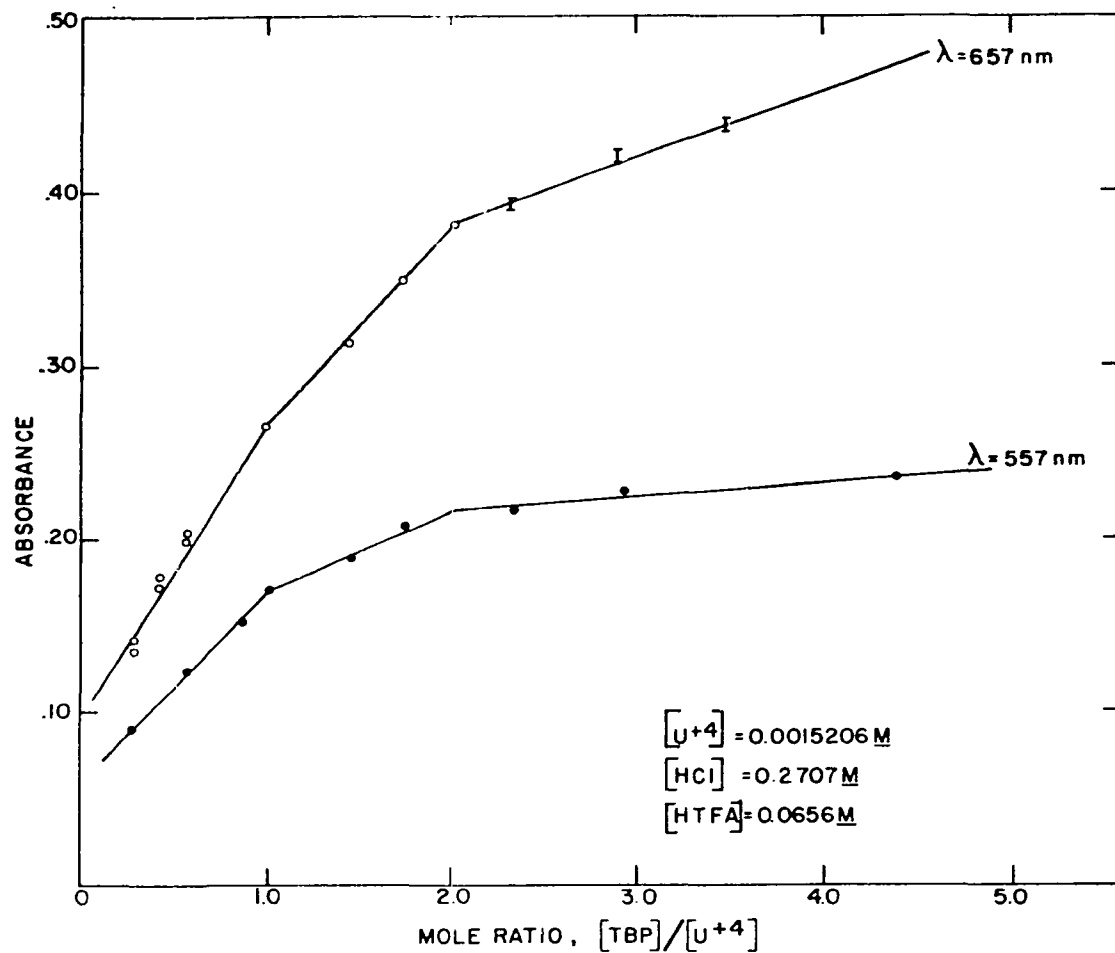


Figure 37. Dependence of the absorbance of the organic phase on the mole ratio, $[TBP]_o/[U^{+4}]_{initial}$, in the system U(IV)-HTFA-TBP-cyclohexane

Thermal Behavior of Fluorinated β -Diketone-Organophosphorus
Adduct Complexes

The thermal instability of certain β -diketone chelates has been attributed to the presence of waters of hydration (24,25,86). The unsuccessful elution of the neodymium(III) chelate of HTFA from a gas chromatographic column was attributed to thermal degradation which was postulated to be related to the presence of hydrated water (113).

Thermograms of the hydrated HTFA and HHFA chelates of Nd(III), Eu(III) and Tm(III) are shown in Figure 38. The loss of hydrated water and subsequent extensive decomposition is seen to occur for these trihydrated chelates.

The thermograms of the corresponding adduct complexes of HTFA-TBP and HHFA-TBP chelates are shown in Figures 39 and 40. A distinct improvement in the thermal stability and in the volatility of the adduct complexes is shown. Since waters of hydration were replaced during the adduct formation with TBP, these thermograms of the adduct complexes provide supporting evidence that hydrated water is instrumental in the thermal degradation of β -diketone chelates of the rare earths.

Thermograms of the fluorinated phosphate adducts of rare earth hexafluoroacetyl acetonates are shown in Figures 41 and

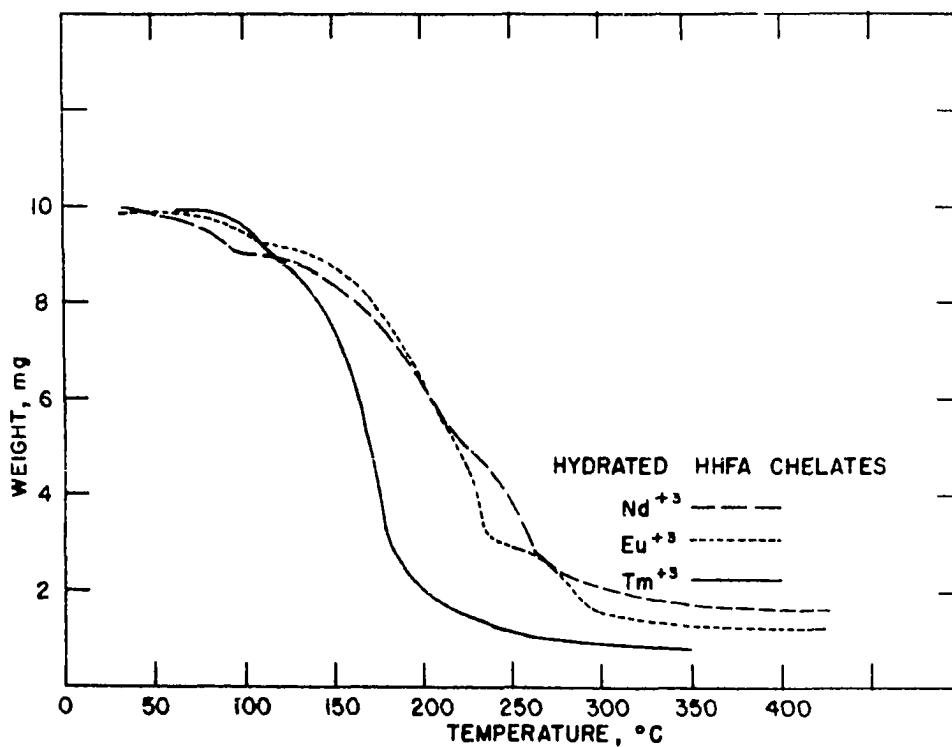
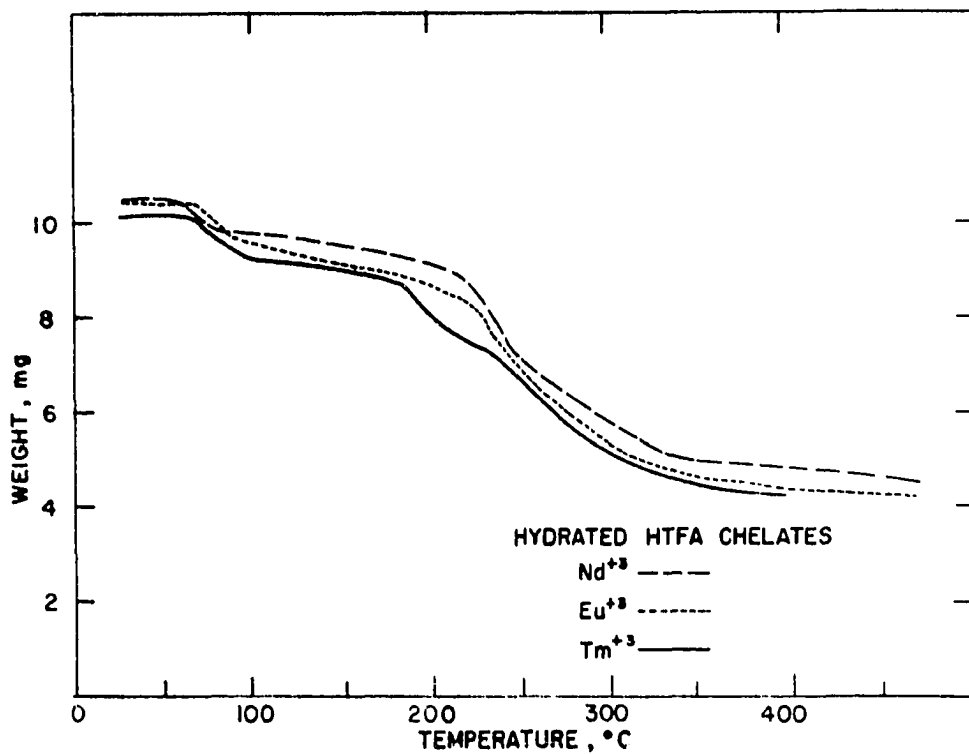


Figure 38. Thermograms of HTFA and HHFA chelates of Nd(III), Eu(III) and Tm(III)

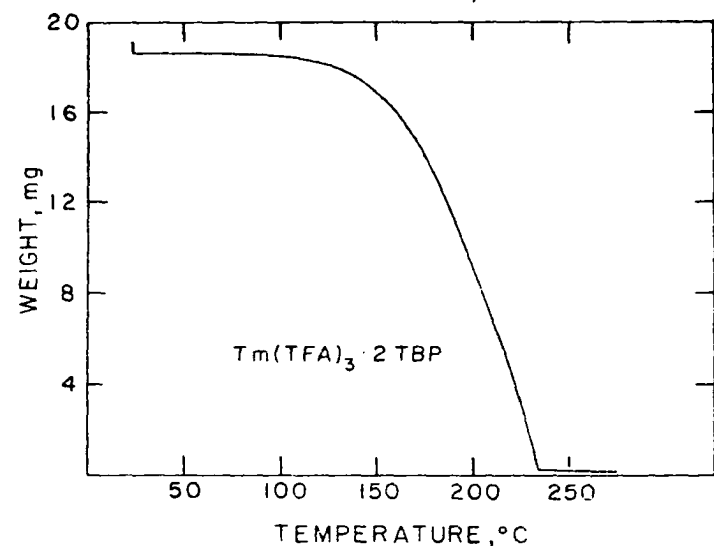
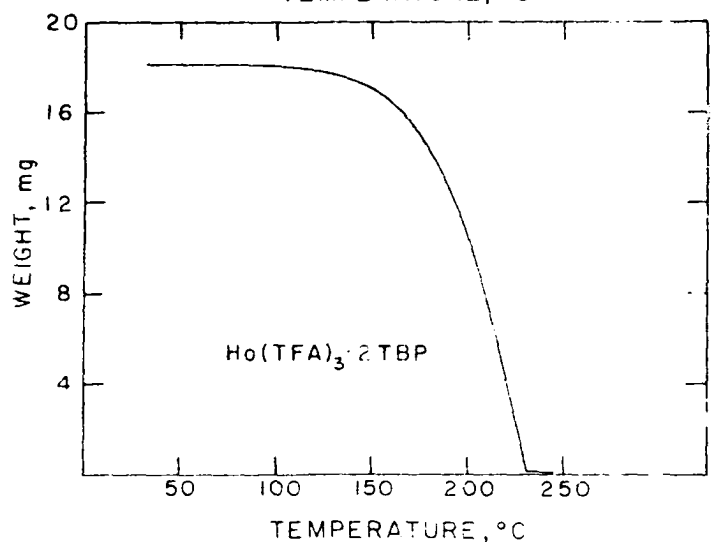
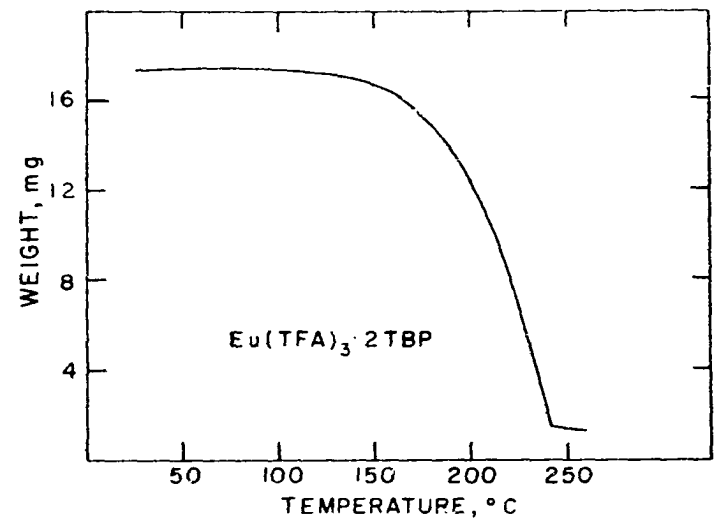
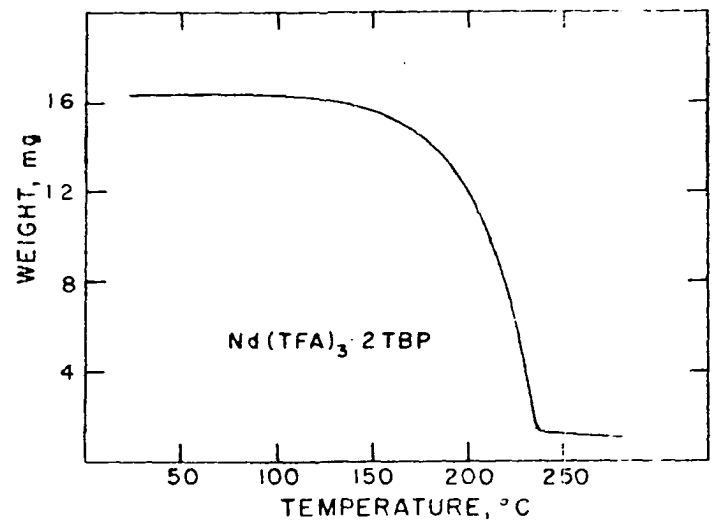


Figure 39. Thermograms of rare earth chelates of HTFA and TBP

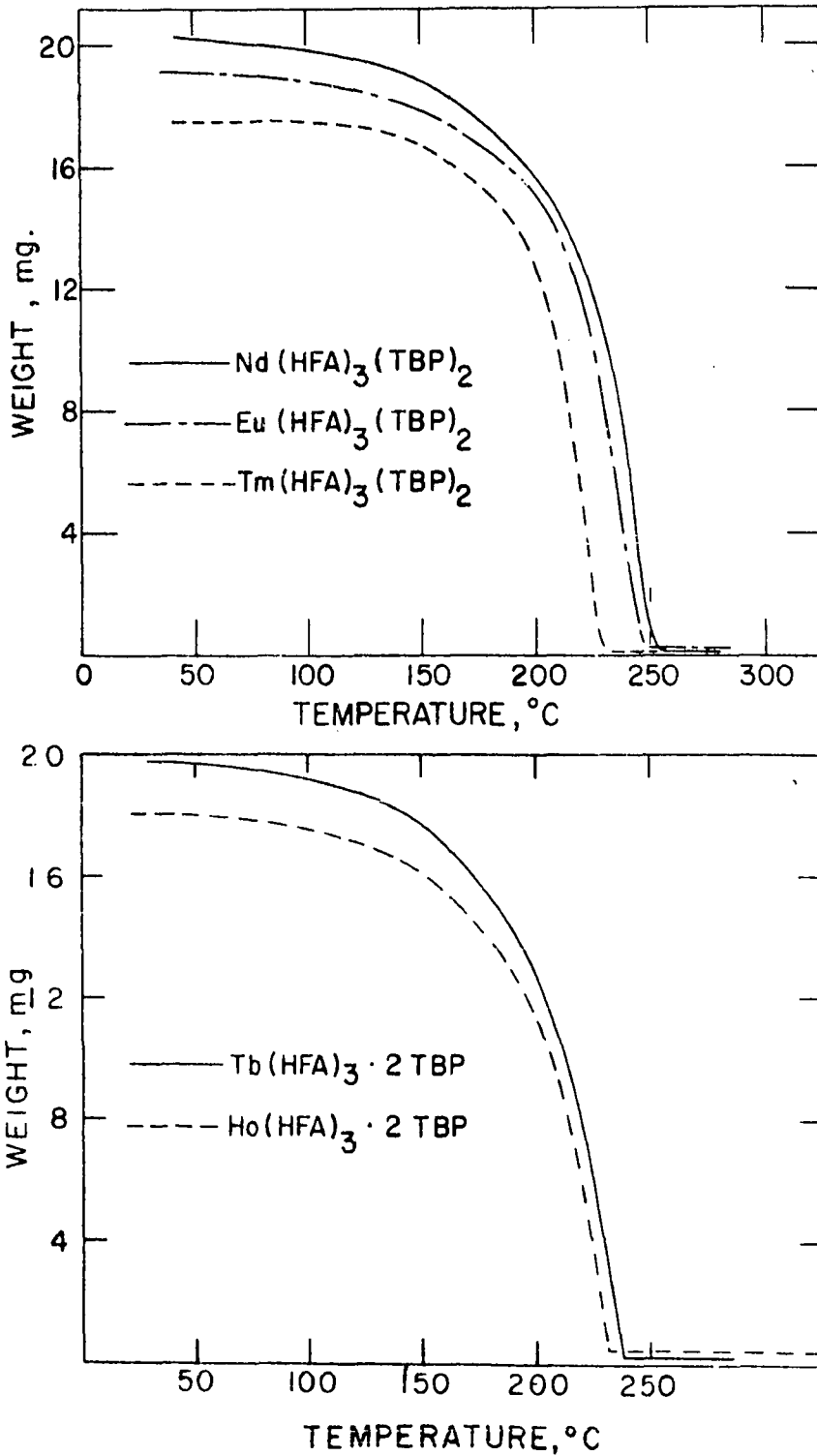


Figure 40. Thermograms of rare earth chelates of HHFA and TBP

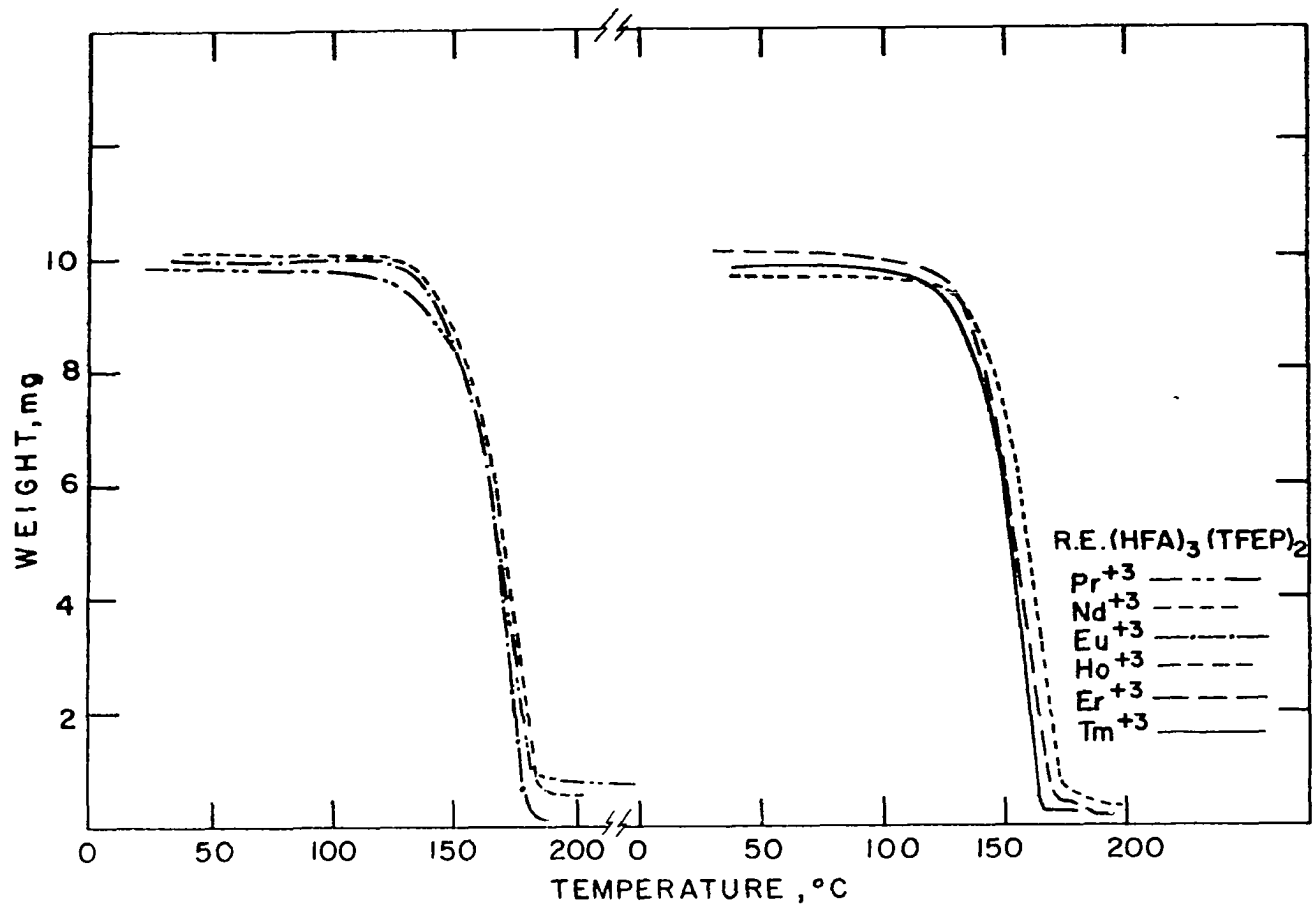


Figure 41. Thermograms of rare earth chelates of HHFA and TFEP

42. The R.E.(HFA)₃(TFEP)₂ chelates volatilized at lower temperatures than the corresponding adducts of TBP. Similar properties were observed for the R.E.(HFA)₃(PFPP)₂ complexes. Although the fluorinated phosphates formed more volatile adduct complexes than TBP, the adduct formation and extraction properties of these compounds were found to be inferior to those of TBP.

The thermograms of the uranyl chelates shown in Figure 43 indicate a greater volatility and thermal stability of UO₂(HFA)₂TBP than is observed for the chelate of HTFA. The anhydrous UO₂(TFA)₂·TBP complex was 70% volatilized between the interval, 150 to 250°C. The corresponding chelate of HHFA began to volatilize at 100°C and reached 95% volatilization at 213°C.

The thermogram of UO₂(TFA)₂TBP indicates that factors other than thermal degradation initiated by hydrated water must also contribute to the instability of the uranyl chelates. Uranium(IV)-chelates were studied in order to test the hypothesis that the presence of the uranyl oxygen atoms could stimulate thermal decomposition by initiating the formation of stable uranium oxides. The thermograms in Figure 44 showed that more volatile and thermally stable complexes of uranium

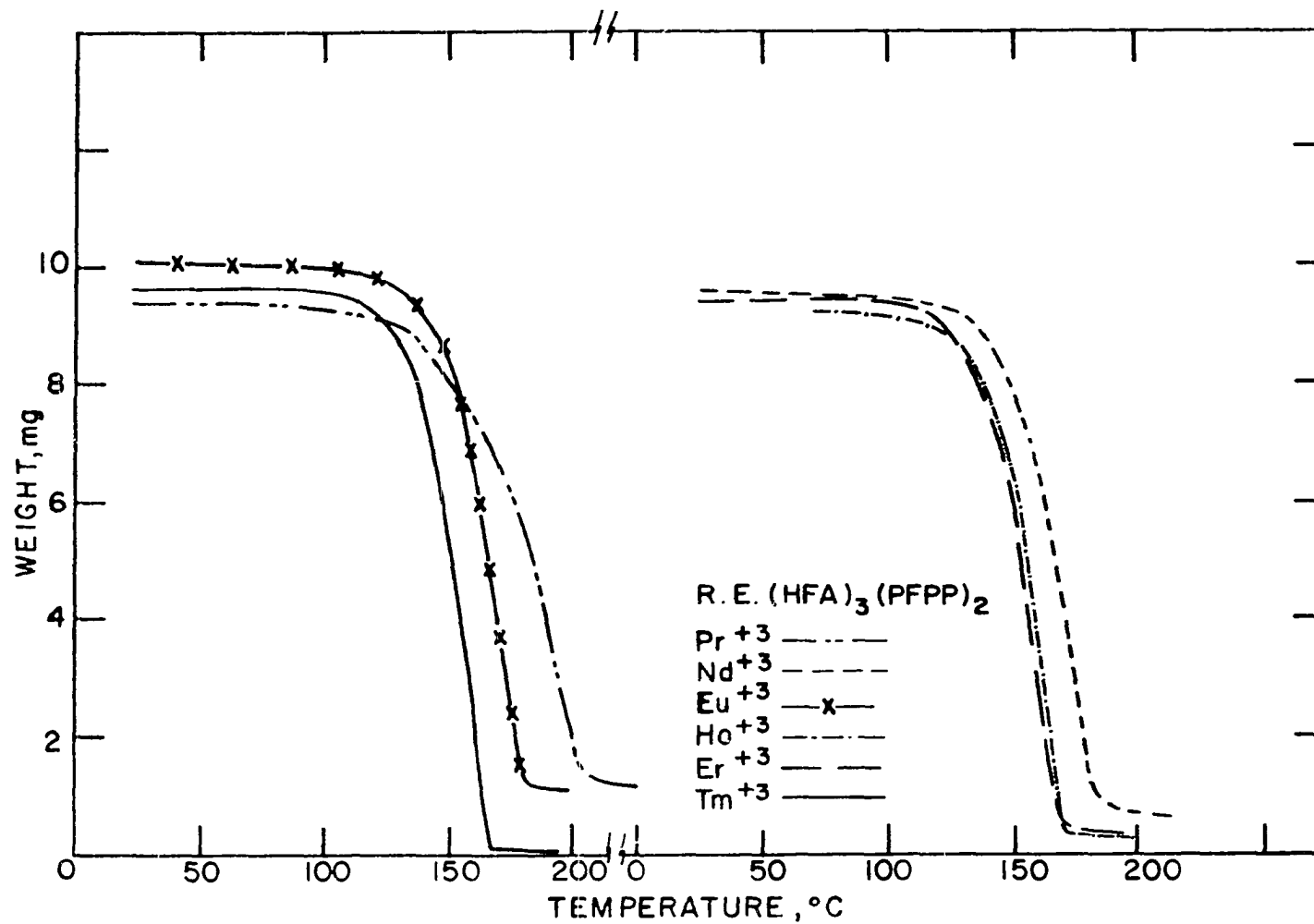


Figure 42. Thermograms of rare earth chelates of HHFA and PFPP

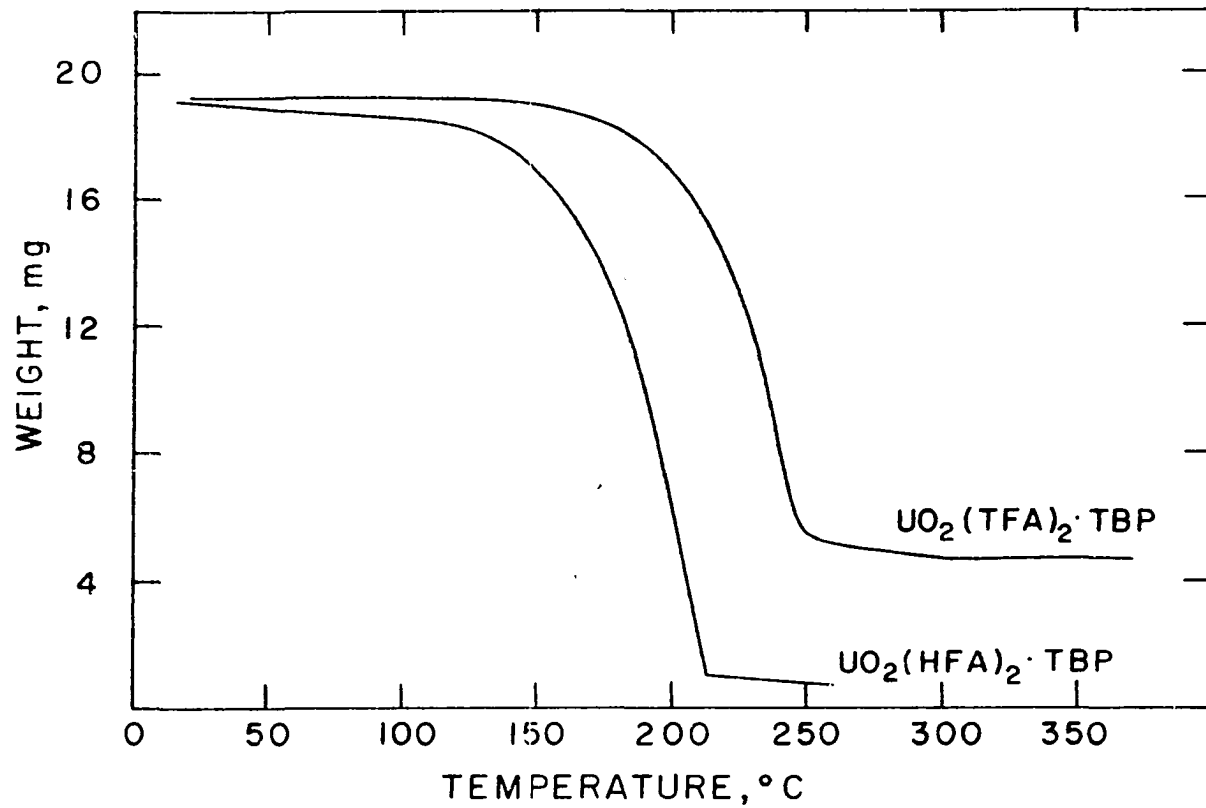


Figure 43. Thermograms of uranyl chelates of HTFA-TBP and HHFA-TBP

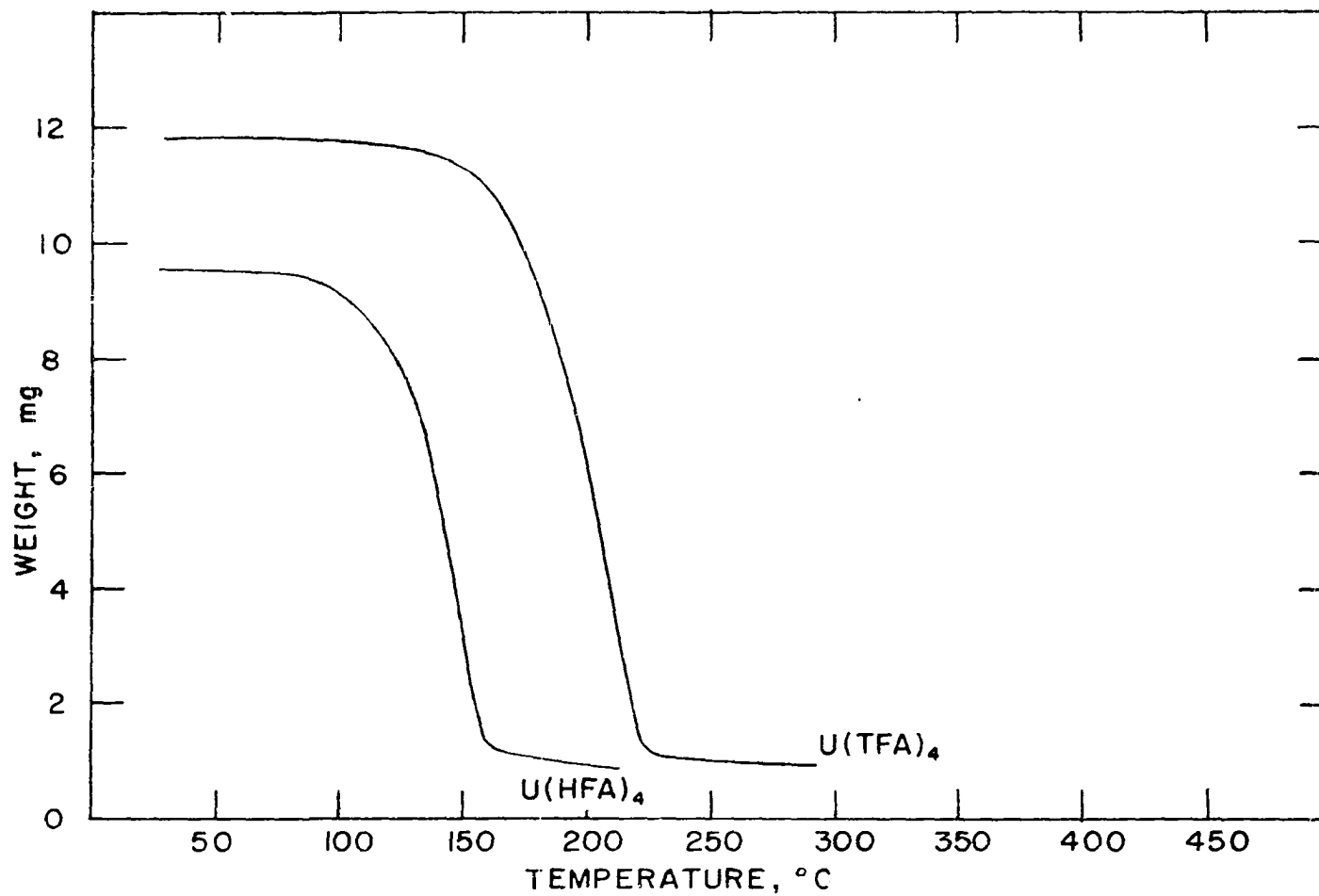


Figure 44. Thermograms of HTFA and HHFA chelates of uranium(IV)

were obtained by a reduction of UO_2^{+2} to U^{+4} . Eighty-eight percent volatilization of $\text{U}(\text{TFA})_4$ occurred over the temperature range 125 to 225°C. The $\text{U}(\text{HFA})_4$ complex was volatilized to the extent of 90% at 170°C.

The poor thermal stability of the fluorinated phosphate derivatives of U(VI) and Th(IV) is shown in Figure 45. The extreme instability of the uranyl complexes probably resulted from a poor thermodynamic stability of the fluorinated phosphate adducts.

Although complete volatilization was not obtained under conditions of thermogravimetry, no evidence of thermal decomposition was found during the gas chromatography of $\text{U}(\text{TFA})_4$ and $\text{U}(\text{HFA})_4$. In Figure 46 well defined peaks for these chelates are shown. The $\text{U}(\text{HFA})_4 \cdot 2\text{TBP}$ complex was eluted at 183°C with tailing, while the $\text{U}(\text{TFA})_4 \cdot 2\text{TBP}$ complex appeared to have decomposed during gas chromatography. To the knowledge of the author the gas chromatography of U(IV)-chelates has not been previously reported. The improved thermal stability of adduct complexes, the rapid quantitative extraction and selective separation capabilities of synergic systems substantiate the claim that the use of mixed ligand systems as gas chromatographic reagents offers significant advantages for inorganic gas chromatography.

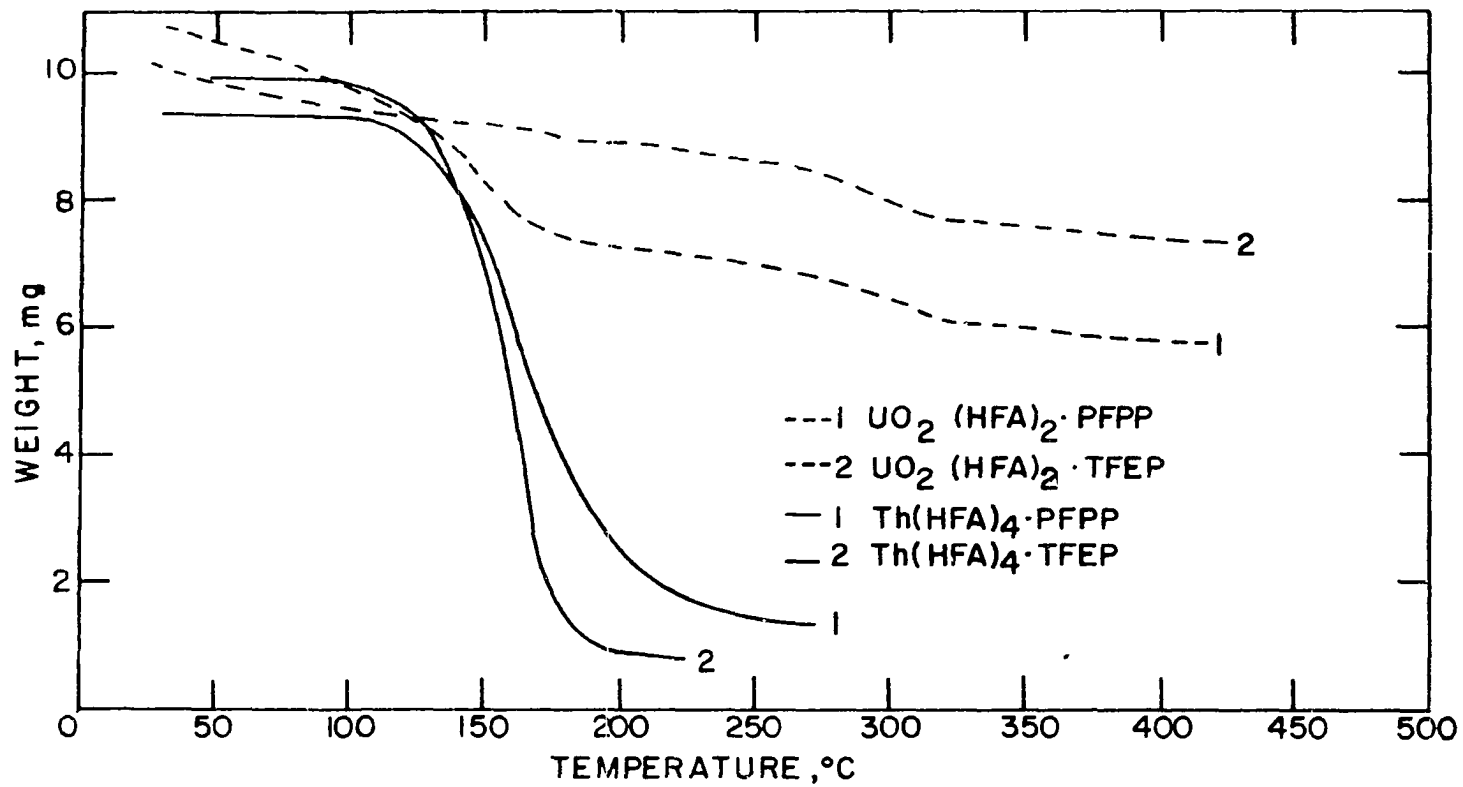


Figure 45. Thermograms of the HHFA-TFEP and HHFA-PFPP chelates of uranium(VI) and thorium(IV)

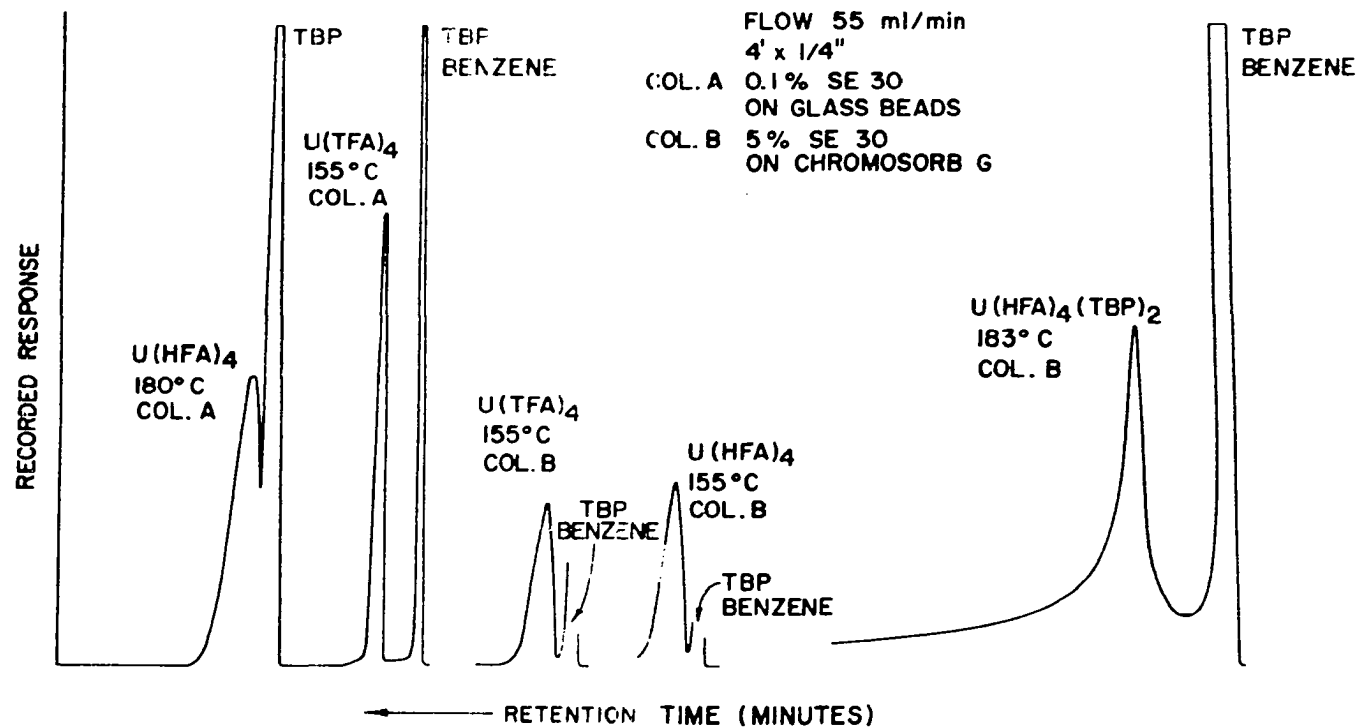


Figure 46. Gas chromatograms of uranium(IV)-chelates of HTFA, HHFA and HHFA-TBP

SUMMARY

The synergic extraction of lanthanides from an aqueous acetate-chloride medium into cyclohexane solutions containing mixtures of the fluorinated β -diketones, trifluoroacetylacetone (HTFA), hexafluoroacetylacetone (HHFA), 8,8,8,7,7,6,6-heptafluoro-2,2-dimethyl-3,5-octanedione (HFOD) and tri-n-butylphosphate (TBP) was studied. Extraction properties of the compounds, 1,1,1,5,5,6,6,7,7,7-decafluoro-2,4-heptanedione (HFHD), 1,1,1,2,2,6,6,7,7,8,8,8-dodecafluoro-3,5-octanedione (HDODEFOD), tri(2,2,2-trifluoroethyl)phosphate (TFEP) and tri(3,3,3,2,2-pentafluoropropyl)phosphate (PFPP) were also investigated. Mole ratio studies and measurements of the dependence of the distribution equilibria on pH, ligand and donor concentrations indicated that species of composition, $R.E.(A)_3 \cdot 2TBP$, were extracted into the organic phase. Most of the desirable extraction properties of a gas chromatographic reagent were shown to be possessed by the system HHFA-TBP-cyclohexane. Rare earth cations at micro and macro levels (10^{-8} to 10^{-2} M) were rapidly and quantitatively converted to the corresponding mixed chelates at a low pH which precluded the hydrolysis of these cations. The stoichiometry of the mixed complexes of HHFA-TBP remained constant during the

extraction process and was identical for the lanthanide series.

The utility of the extraction systems, HTFA in benzene, HTFA-TBP in cyclohexane and HHFA-TBP in cyclohexane, for quantitative separations was demonstrated. Scandium(III) and Fe(III) were easily separated from the rare earths by extraction with benzene solutions of HTFA. Rare earths were quantitatively separated from Al(III) by extraction with HHFA-TBP in cyclohexane. A large excess of UO_2^{+2} ($\leq 1.25 \times 10^3$ [R.E.]) and Th(IV) ($\leq 3.25 \times 10^2$ [R.E.]) was separated from small quantities of rare earths (10^{-5} M) by multiple extractions with HTFA-TBP in cyclohexane. The extent of extraction of U(IV) from HCl solutions indicated that the highly fluorinated β -diketones in the presence of TBP are useful for the separation of quadrivalent cations from the lanthanide elements.

Available information on the extraction of cation by HTFA was included in the LITERATURE REVIEW of this thesis. This information and the distribution curves measured during this study provide a basis for the choice of conditions for the separation of various cations from each other and from the rare earths. The lanthanides can be selectively extracted by combining an initial extraction using HTFA in benzene to remove common impurity elements, with a subsequent extraction

of the lanthanides by HTFA-TBP or HHFA-TBP in cyclohexane.

The extraction constants obtained for the synergic extraction of the lanthanides by mixtures of fluorinated β -diketones and TBP increased in the order HTFA < HFOD < HHFA << HFHD. Although Eq. 24 shows the dependence of the overall equilibrium process on several factors, the cubic dependence on the acid dissociation constant should be significant. The variation of the pK_a values with structure in this series of β -diketones is respectively, 6.42, 3.52, 4.64 and 3.32. Except for the bulky HFOD ligand containing the large hydrocarbon group, the observed order is in agreement with the extraction constants. No significant difference in the adduct formation of rare earth chelates of HHFA and HFHD with TBP occurred. Apparently no important steric effects or changes in Lewis acidity of the chelates of these highly acidic, fully fluorinated, straight chain β -diketones occurred.

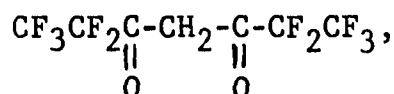
Relative trends in the thermal stability and volatility of chelates of the lanthanide and some related elements were obtained from thermogravimetric analysis of the hydrated and mixed chelates. Marked improvements in thermal stability were obtained by displacement of hydrated water during adduct formation with TBP. The volatilization at low temperature and

the thermal stability of adduct complexes with respect to fragmentation and decomposition is obviously important in the gas chromatography of metal chelates. However, TGA studies of the hydrated HHFA and HTFA chelates and of the respective non-hydrated adduct complexes with TBP revealed that volatility without apparent thermal degradation did not guarantee gas chromatographability. The temperatures at which volatilization occurred and the thermal stability of the HTFA-TBP and HHFA-TBP chelates were similar, however the former complexes have not been successfully gas chromatographed. Although the exact nature of the inability to chromatograph the rare earth chelates of HTFA-TBP has not been defined, it may be related to the lower thermodynamic stability of the HTFA-TBP complexes. The known chromatographability of the HHFA and HFHD adduct complexes of TBP suggests that other volatile chelating ligands with pK_a values ≤ 5.0 should form adduct complexes which are stable enough for the gas chromatography of the rare earths. Thermograms of the mixed chelates of HHFA and TFEP or PFPP showed an increase in volatility of the adducts upon substitution of the fluorinated phosphates for TBP. However, the improved volatility was offset by a corresponding loss in extraction power. The chelates, $U(TFA)_4$, $U(HFA)_4$ and

$U(HFA)_4(TBP)_2$ were successfully gas chromatographed without any apparent decomposition.

SUGGESTIONS FOR FUTURE WORK

Gas chromatographic data already obtained for mixed chelates of the rare earths indicate that mixed complexes of dissymmetrical β -diketones were not as readily chromatographed as those of symmetrical ligands. In view of this desirable structural feature, one would expect the β -diketone,



to also be useful as a gas chromatographic reagent. This ligand contains the same number of fluorinated carbon atoms as HFHD and fewer than HDODEFOD. It should therefore form more soluble mixed complexes than the latter and retain the adduct stability and extraction characteristics of the former.

Because of the inability to obtain pure HDODEFOD, study of this ligand was restricted to a few comparative experiments. If future preparations of the new ligand and HDODEFOD can be made to yield pure fractions, the pKa of these β -diketones and the efficiency of the extraction of rare earths in synergic systems using these ligands should be undertaken.

In view of the successful separation of UO_2^{+2} from lanthanides by extraction with HTFA-TBP in cyclohexane, one might predict that other actinides including PuO_2^{+2} , NpO_2^{+2} and AmO_2^{+2} can be separated from lanthanides with this reagent.

The high solubility of the $\text{UO}_2(\text{TFA})_2\text{TBP}$ complex and the negligible loss of rare earth during multiple extraction suggests that the HTFA-TBP-cyclohexane system would be suitable for separation of these elements from lanthanides using techniques of counter current solvent extraction.

A detailed investigation of the influence of uranyl oxygens and acetate complexation on the adduct formation of uranium(VI) with TBP could determine the relative importance of these two effects. Experiments using uranium isotopes could be designed to study the effect of acetate concentration on the HTFA-TBP and HHFA-TBP equilibria. Measurements of aqueous phase stability constants of the UO_2A^+ and UO_2A_2 complexes where A is the anion of HTFA and HHFA, would allow calculation of the relative concentrations of the uranyl chelate ions in the presence of acetate. From calorimetric measurements of the heat of adduct formation of $\text{UO}_2(\text{TFA})_2$ and $\text{UO}_2(\text{HFA})_2$ with TBP or a series of donor molecules in cyclohexane or another non-specific interacting solvent, one should be able to determine the relative acceptor strengths of the respective chelates.

On the basis of the extraction data shown in this thesis and the demonstrated gas chromatographability of chelates in

the literature, several systems can be suggested for initial studies of the quantitiveness of the gas chromatography of metal chelates. Figure 28 indicates that Th(IV) can be quantitatively extracted and separated from rare earths at pH 3.0 with HTFA in benzene. The resulting $\text{Th}(\text{TFA})_4$ chelate is reported to be anhydrous and completely volatile (11). Scandium(III) and Fe(III) were separated from rare earths. The resulting HTFA chelates of these metals are reported to be easily chromatographed. Thus, samples containing rare earths and common impurity elements that can be separated by extraction and are known to be chromatographable as the HTFA chelates, are amenable to analysis by gas chromatography.

Rare earths were separated from aluminum by extraction with HHFA-TBP. A similar separation from calcium and other elements was indicated by extraction curves. The perfection of the quantitative gas chromatography of the mixed rare earth chelates should allow the analysis of alloy samples containing heavy rare earths and non-transition or transition elements that are separable during the solvent extraction or gas chromatographic processes.

It would be interesting to examine the possibility of using gas chromatography for the simultaneous analysis of a given cation in different valence states. When a cation is

present in the trivalent and divalent states, the tris chelate and bis complex should have different volatilities and retention times. In the case of a non-adduct forming tris chelate and a chromatographable mixed divalent complex, the separation of the two chelates of the cation in different valence states should be easily accomplished.

The substitution of TFEP and PFEP for TBP was shown to increase the volatility of the rare earth chelates. However, a decrease in the solubility of the adduct complex in cyclohexane occurred. Other longer chain fluorophosphates and a fluorinated phosphine oxide are available. Synergic extraction systems in which fluorinated cyclohexane or a fluorocarbon solvent are employed could result in an increase in the solubility of the highly fluorinated mixed chelates.

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APPENDIX

Table 19. Properties of organic reagents

Compound	Mol. weight	Density ^a g/ml at 25°C	Boiling point ^b °C	K _D (cyclohexane, H ₂ O)
HAA	100.12	0.976	135° at 745 mm	---
HTFA	153.99	1.263	107	0.045, pH 1.22-5.58
HHFA	208.06	1.465	70	0.0068, pH ≤ 3.88
HFOD	296.10	1.300	68-69 at 20 mm	>100, pH 1.2-5.6
HDODEFOD	358.07	1.537	---	---
HFHD	308.07	1.452	72	---
TBP	266.32	0.976	185-189 at 20 mm	870 (2)
TFEP	344.07	1.575	84-85 at 10 mm	2.32, pH 3.18
PFPP	493.99	1.627	94 at 10 mm	---

^aAverage values obtained from duplicate pycnometrical measurements or duplicate weighings of 5 or 10 ml of the compounds in volumetric flasks.

^bValues reported in the literature or recorded by John J. Richard.

Table 20. Extraction constants for Nd(III), Eu(III) and Tm(III) in the system HHFA-TBP in cyclohexane

log K _{eq}	Nd(III)		log K _{eq}	Eu(III)		log K _{eq}	Tm(III)	
	[TBP] ₀ ² (x10 ⁶)	K _D (x10 ²)		[TBP] ₀ ² (x10 ⁶)	K _D (x10 ²)		[TBP] ₀ ² (x10 ⁶)	K _D (x10 ²)
4.333	1.735	0.80	5.029	0.720	1.14	4.684	0.77	2.23
4.334	4.810	2.22	5.025	1.735	2.55	4.607	1.735	4.21
4.463	13.85	8.61	5.013	4.810	6.87	4.629	4.810	12.3
4.253	77.00	29.5	5.133	13.85	25.9	4.714	13.85	43.0
4.35 ave.			4.887 ^a	77.00	82.2	4.502	77.00	147
			5.05 ave.			4.63 ave.		

Conditions

[HHFA] ³ = 2.74 x 10 ⁻⁶ M	[HHFA] ³ = 2.74 x 10 ⁻⁶ M	[HHFA] ³ = 2.74 x 10 ⁻⁶ M
[H] ³ = 12.8 x 10 ⁻⁶ M	[H] ³ = 1.97 x 10 ⁻⁵ M	[H] ³ = 4.54 x 10 ⁻⁶ M

^aOmitted in calculation of average log K_{eq}.

Table 21. Extraction constants for Nd(III), Eu(III) and Tm(III) in the system, HTFA-TBP in cyclohexane

log K_{eq}	Nd(III) $[TBP]_O^2$ ($\times 10^4$)	K_D ($\times 10^2$)	log K_{eq}	Eu(III) $[TBP]_O^2$ ($\times 10^4$)	K_D ($\times 10^2$)	log K_{eq}	Tm(III) $[TBP]_O^2$ ($\times 10^4$)	K_D ($\times 10^2$)
-2.670	0.680	0.680	-2.109	0.1925	0.086	-2.449	1.740	0.4670
-2.755	1.58	1.58	-2.159	0.7690	0.306	-2.406	4.831	1.43
-2.803	5.65	5.65	-2.190	1.730	0.639	-2.587	19.33	3.78
-2.865	11.0	11.0	-2.327	4.820	1.30	-2.685	43.48	6.78
-2.77			-2.291	19.25	5.64	-2.853	214.6	22.7
			-2.22 ave.			-2.763	1933	25.2
						-2.62 ave.		

Conditions

$$[HTFA]^3 = 1.042 \times 10^{-4} \underline{M}$$

$$[H]^3 = 5.61 \times 10^{-9} \underline{M}$$

$$[HTFA]^3 = 1.042 \times 10^{-4} \underline{M}$$

$$[H]^3 = 1.82 \times 10^{-9} \underline{M}$$

$$[HTFA]^3 = 1.042 \times 10^{-4} \underline{M}$$

$$[H]^3 = 1.38 \times 10^{-9} \underline{M}$$

Table 22. Extraction constants for Nd(III), Eu(III) and Tm(III) in the system, HFHD-TBP in cyclohexane

log K_{eq}	Nd(III)		log K_{eq}	Eu(III)		log K_{eq}	Tm(III)	
	$[TBP]_O^2$ ($\times 10^8$)	K_D ($\times 10$)		$[TBP]_O^2$ ($\times 10^8$)	K_D		$[TBP]_O^2$ ($\times 10^8$)	K_D ($\times 10$)
10.02	0.193	3.25	11.01	0.193	3.23	10.451	0.183	1.163
9.980	0.422	6.53	11.07	0.422	8.03	10.462	0.422	2.604
9.941	0.744	10.5	10.96	0.744	11.1	10.501	1.745	11.78
9.882	1.75	21.6	10.98	1.745	27.3	10.47 ave.		
9.980	4.83	69.3	11.08	4.82	95.5			
9.95 ave.			11.03 ave.					
Conditions								
$[HFHD]^3 = 8.35 \times 10^{-7} \underline{M}$			$[HFHD]^3 = 8.35 \times 10^{-7} \underline{M}$			$[HFHD]^3 = 8.35 \times 10^{-7} \underline{M}$		
$[H]^3 = 5.15 \times 10^{-5} \underline{M}$			$[H]^3 = 5.15 \times 10^{-5} \underline{M}$			$[H]^3 = 3.92 \times 10^{-5} \underline{M}$		

Table 23. Extraction constants for Nd(III), Eu(III) and Tm(III) in the system, HFOD-TBP in cyclohexane

log K_{eq}	Nd(III)		log K_{eq}	Eu(III)		log K_{eq}	Tm(III)	
	$[HFOD]_O^3$ ($\times 10^6$)	K_D ($\times 10^2$)		$[HFOD]_O^3$ ($\times 10^6$)	K_D ($\times 10^2$)		$[HFOD]_O^3$ ($\times 10^6$)	K_D ($\times 10^2$)
1.749	2.605	2.54	1.939		3.41	1.731	1.099	0.677
1.661	13.96	11.1	1.897	2.605	16.6	1.517	2.605	0.980
1.669	40.71	33.0	1.972	13.96	57.4	1.793	13.96	19.91
1.647	70.34	54.3	1.977	40.71	100	1.745	40.71	26.1
1.548	137.4	84.4	1.948	70.34	183	1.859	70.34	58.1
1.592	325.7	221	1.927	137.39	414	1.768	237.4	159
1.64 ave.			ave. 1.94	325.7		1.74 ave.		

Conditions:

$$[TBP]_O^2 = 1.740 \times 10^{-4} \text{ M}$$

$$[TBP]_O^2 = 1.740 \times 10^{-4} \text{ M}$$

$$[TBP]_O^2 = 1.740 \times 10^{-4} \text{ M}$$

$$[H]^3 = 1.00 \times 10^{-6} \text{ M}$$

$$[H]^3 = 1.16 \times 10^{-6} \text{ M}$$

$$[H]^3 = 1.52 \times 10^{-6} \text{ M}$$

Table 24. Extraction constant for Nd(III) in the system,
HHFA-TFEP in cyclohexane

$\log K_{eq}$	$\frac{[TFEP]_o^2}{\times 10^4}$	K_D
-0.223	0.3944	0.122
-0.261	0.8798	0.250
-0.237	1.588	0.478
-0.24 ave.		

Conditions:

$$[HHFA]^3 = 7.89 \times 10^{-6} \text{ M}$$

$$[H]^3 = 1.52 \times 10^{-9} \text{ M}$$

Buffer Solutions for the Adjustment of pH
During the Separation of Cations

The separation of cations by solvent extraction in chelating systems is often critically dependent on the equilibrium pH. Although the initial pH depends only on the pK_a , P_{HA} , $[HA]_0$ and buffer, the pH at equilibrium can be lower than the initial pH because n equivalents of H^+ are generated during the extraction. The symbol, n , is the charge on the cation. In order to maintain the pH in a desired region, buffer solutions must be chosen with regards to the initial concentration of the cation in the aqueous phase. The results of preliminary experiments to determine the pH of various sodium acetate-acetic acid buffers to which known concentrations of HCl were added are shown in Table 25. These results aided in choosing appropriate buffer solutions for the control of pH in aqueous phases containing known quantities of metal cations. Solutions 0.05 M in HCl were prepared by diluting 0.5-ml of 1.0 M HCl to 10-ml with buffer solutions 1 to 4. The measured pH values were 1.47, 1.76, 3.98 and 4.53, respectively.

A 10-ml solution of 0.03 M HCl, which also contained 0.3 ml of buffer 5, was found to have a pH of 4.35. When 4-ml of

this buffer and appropriate amounts of HCl were added to obtain 10-ml of a solution 0.05 M in HCl, the pH was found to be 4.05.

Table 25. Buffer solutions of sodium acetate and acetic acid

Buffer number	pH of buffer		pH of solutions containing HCl and buffer ^a		
	calc.	measured	0.05 <u>M</u> HCl	0.005 <u>M</u> HCl	0.001 <u>M</u> HCl
1	3.42	3.35	1.37	2.52	3.34
2	4.05	4.05	1.50	3.65	4.05
3	4.63	4.58	1.78	4.47	4.68
4	5.23	5.22	2.18	5.00	5.17
5	5.89	5.89	2.48	--	--

^aSolutions were prepared by adding 3 ml of buffer, known amounts of HCl and diluting to 10-ml.

Aqueous phases of Nd(III) and Al(III) were prepared by adding appropriate aliquots of the solutions of the cations and 5-ml of a sodium acetate-HCl buffer of pH 3.52 and by diluting to a volume of 25 ml. The pH of these solutions and conditions for the preparation of other solutions are shown in Table 26. The equilibrium pH of a solution 1.18×10^{-2} M in Al(III) and 1.217×10^{-2} M in Nd(III) was maintained at 3.01 by adding appropriate aliquots of the solutions of Al and Nd and by diluting the mixture to a volume of 25-ml with buffer solution 3.

Table 26. Conditions for pH control during the separation of cations

[Al(III)]	[Nd(III)]	pH _(initial)	pH _(equilibrium)
1.18×10^{-2} <u>M</u>	1.217×10^{-2} <u>M</u>	3.20	1.63
"	" $\times 10^{-3}$ <u>M</u>	3.40	2.68
"	" $\times 10^{-5}$ <u>M</u>	3.45	3.11

[Sc(III)]	[Tm(III)]	Buffer ^a	pH _(equilibrium)
0.015 <u>M</u>	8.64×10^{-5} <u>M</u>	7 ml of 3	3.60
2.46×10^{-3} <u>M</u>	" $\times 10^{-5}$ <u>M</u>	4 ml of 2	3.42
"	" $\times 10^{-5}$ <u>M</u>	3 ml of 1	2.86

[Fe(III)]	[Eu(III)]	Buffer ^a	pH _(equilibrium)
1.00×10^{-2} <u>M</u>	1.032×10^{-5} <u>M</u>	6 ml of 3	2.62
" $\times 10^{-3}$ <u>M</u>	" $\times 10^{-4}$ <u>M</u>	4 ml of 2	3.06
" $\times 10^{-4}$ <u>M</u>	1.096×10^{-2} <u>M</u>	4 ml of 2	3.08
$< 10^{-6}$ <u>M</u>	$\approx 10^{-8}$ <u>M</u>	4 ml of 1	2.45

^aAqueous phase volume of 10-ml.

The equilibrium pH of a solution 0.05 M in UO_2^{+2} and also 4×10^{-5} M in total rare earth was controlled at 1.02. The original aqueous phase was prepared by adding the appropriate amounts of solutions of UO_2^{+2} ; aliquots of the rare earths and 8-ml of buffer 4. This mixture was diluted to ~20-ml, the pH was adjusted to 1.78 with dilute HCl, and the solution was diluted to a final volume of 25-ml. Solutions which were 1.21×10^{-3} M in Th(IV) and 4×10^{-5} M in rare earths were prepared in the same manner as previously described. The initial pH was adjusted to 1.10 with HCl and the mixture was diluted to a final volume of 25-ml. An equilibrium pH of 1.10 to 1.09 was found.

Derivation of Extraction Equations

Equation (9)

By definition the distribution ratio of a β -diketone chelate is given as

$$K_D^o = \frac{[MA_n]_o}{[M] + \sum_{n=1}^n [MA_n]} \quad . \quad (A)$$

Substitution into Eq. (A) for quantities given by the partition coefficient, $[MA_n]_o = P_{MA_n} [MA_n]$ and the stability constants, $\beta_1, \beta_2 \dots, \beta_n$, produces

$$K_D^o = \frac{P_{MA_n} \beta_n [A]^n}{1 + \sum_{n=1}^n \beta_n [A]^n} \quad . \quad (B)$$

Since $[A]$ is given by the acid dissociation constant, $[A] = K_a [HA] / [H^+]$, Eq. (B) can be rearranged to

$$K_D^o = \frac{P_{MA_n} \beta_n K_a^n [HA]^n}{[H]^n (1 + \sum_{n=1}^n \beta_n [A]^n)} \quad . \quad (C)$$

If the expression, $[HA] = [HA]_o / P_{HA}$, is substituted into Eq. (C), the equation for the distribution ratio becomes

$$K_D^o = \frac{P_{MA_n} \beta_n K_a^n [HA]_o^n}{[H]^n P_{HA}^n (1 + \sum_{n=1}^n \beta_n [A]^n)} \quad .$$

The equilibrium constant,

$$K_{\text{eq}}^{\circ} = \frac{K_{\text{D}}^{\circ} [\text{H}]^3}{[\text{HA}]_0^3}, \quad (\text{D})$$

then becomes

$$K_{\text{eq}}^{\circ} = \frac{P_{\text{MA}_n} \beta_n K_a^n}{P_{\text{HA}}^n (1 + \sum_{n=1}^n \beta_n [\text{A}]^n)} \quad (\text{9})$$

upon substitution for K_{D}° into Eq. (D).

Equation (13)

If $[\text{Org}]$ and $[\text{Aq}]$ are the concentrations of the distributing species in the organic and aqueous phases, respectively, the distribution ratio is given by

$$K_{\text{D}} = \frac{[\text{Org}]}{[\text{Aq}]}. \quad (\text{A})$$

By definition

$$E = \frac{[\text{Org}]100}{[\text{Org}]+[\text{Aq}]}. \quad (\text{B})$$

Substitution into Eq. (B) for K_{D} and rearrangement gives

$$E = \frac{K_{\text{D}}[\text{Aq}](100)}{K_{\text{D}}[\text{Aq}]+[\text{Aq}]} = \frac{K_{\text{D}} 100}{K_{\text{D}}+1}, \quad (\text{C})$$

an expression that is applicable for equal volumes of the two phases. In the general form Eq. (C) becomes

$$E = \frac{K_D \cdot 100}{K_D + \frac{V_{aq}}{V_{org}}} \quad (D)$$

Mathematical manipulation of Eq. (C) gives the following:

$$\frac{E}{100} = \frac{1}{1 + \frac{1}{K_D}} \quad \text{and} \quad \frac{100}{E} = 1 + \frac{1}{K_D} ; \quad \frac{1}{K_D} = \frac{100}{E} - 1 = \frac{100 - E}{E} ;$$

$$K_D = \frac{E}{100 - E} \quad \text{and} \quad \log K_D = \log \frac{E}{100 - E} \quad (13)$$

Equation (24)

The principal reaction, $M + nHA(o) + mD(o) \rightleftharpoons MA_nD_m(o) + nH^+$, occurs in the system HA-D-solvent. The corresponding equilibrium constant,

$$K_{eq} = \frac{[MA_nD_m]_o [H]^n}{[M][HA]_o^n [D]_o^m} \quad (A)$$

can be written. Upon substitution of the distribution ratio into Eq. (A) the expression,

$$K_{eq} = \frac{K_D [H]^n}{[HA]_o^n [D]_o^m} \quad (B)$$

is obtained.

By definition the distribution ratio of a cation in a synergic system is

$$K_D = \frac{[MA_n]_o + [MA_n D]_o + \dots + [MA_n D_m]_o}{[M] + [MA] + \dots + [MA_n]} \quad (C)$$

Substitution of the cumulative values of β_n and β_m into Eq.

(C) gives

$$K_D = \frac{[MA_n]_o + \beta_{m=1} [MA_n]_o [D]_o + \dots + \beta_m [MA_n]_o [D]_o^m}{[M] + \beta_{n=1} [M][A] + \dots + \beta_n [M][A]^n} \quad (D)$$

Further rearrangement of Eq. (D) gives

$$K_D = \frac{[MA_n]_o (1 + \sum_{m=1}^m \beta_m [D]_o^m)}{[M] (1 + \sum_{n=1}^n \beta_n [A]^n)} \quad (E)$$

Substitution of these quantities, $[MA_n]_o = P_{MA_n} [MA_n]$, $[MA_n] = \beta_n [M][A]^n$ and K_D into Eq. (B) gives

$$K_{eq} = \frac{P_{MA_n} \beta_n [M] [A]^n [H]^n (1 + \sum_{m=1}^m \beta_m [D]_o^m)}{[HA]_o^n [D]_o^m [M] (1 + \sum_{n=1}^n \beta_n [A]^n)} \quad (F)$$

Upon suitable substitutions into Eq. (F) for

$$[HA]_o = P_{HA} [HA], \quad [HA] = \frac{[H][A]}{K_a} \quad \text{and} \quad [HA]_o^n = \frac{P_{HA}^n [H][A]^n}{K_a^n}$$

Eq. (13),

$$K_{eq} = \frac{P_{MA_n} \beta_n [A]^n (K_a)^n [H] (1 + \sum_{m=1}^m \beta_m [D]_o^m)}{P_{HA} [H][A]^n [D]_o^m (1 + \sum_{n=1}^n \beta_n [A]^n)},$$

is obtained.

Equation 28

$$[\text{HA}]_{\text{T}'} = [\text{HA}]_{\text{o,initial}} - [\text{HA}]_{\text{complexed}} - [\text{A}^-]$$

$$[\text{HA}]_{\text{complexed}} = [\text{MA}^{+2}] + 2[\text{MA}_2^+] + 3[\text{MA}_3]_{\text{o}} + 3[\text{MA}_3\text{D}_2]_{\text{o}}$$

The maximum $[\text{HA}]_{\text{complexed}} = 3[\text{M}^{+n}]_{\text{initial}}$.

If aqueous phase complexation is negligible,

$$[\text{HA}]_{\text{complexed}} = 3[\text{MA}_3\text{D}_2]_{\text{o}} = 3(\text{E}/100) [\text{M}^{+n}]_{\text{initial}}$$

$$[\text{HA}]_{\text{o,initial}} = [\text{HA}]_{\text{o}} + [\text{HA}] + [\text{A}^-]$$

$$= K_{\text{D,HA}} \{ [\text{HA}] + [\text{A}^-] \} + [\text{HA}] + [\text{A}^-]$$

$$= K_{\text{D,HA}} \{ [\text{H}]K_{\text{a}}^{-1}[\text{A}^-] + [\text{A}^-] \} + [\text{H}^+]K_{\text{a}}^{-1}[\text{A}^-] + [\text{A}^-]$$

$$[\text{A}^-] = \frac{[\text{HA}]_{\text{o,initial}}}{K_{\text{D,HA}}[\text{H}^+]K_{\text{a}}^{-1} + K_{\text{D,HA}} + [\text{H}^+]K_{\text{a}}^{-1} + 1}$$

$K_{\text{D,HA}}$ is the distribution ratio of the β -diketone and K_{a} is the acid dissociation constant.

$$[\text{HA}]_{\text{T}'} = [\text{HA}]_{\text{o,initial}} - 3[\text{M}^{+n}]_{\text{initial}} (\text{E}/100)$$

$$- \frac{[\text{HA}]_{\text{o,initial}}}{K_{\text{D,HA}} \{ [\text{H}]K_{\text{a}}^{-1} + 1 \} + [\text{H}^+]K_{\text{a}}^{-1} + 1}$$

Equation 33

The equation for the synergic system that corresponds to Eq. (16) is written as

$$\text{pH}_{1/2} = -\frac{1}{n} \log K_{\text{eq}} - \log[\text{HA}]_0 - \frac{m}{n} \log [\text{D}]_0 . \quad (\text{A})$$

At equal $[\text{HA}]_0$ in the normal and synergic systems, Eq. (16)

and the above can be combined to give

$$\text{pH}_{1/2}^0 + \frac{1}{n} \log K_{\text{eq}}^0 = \text{pH}_{1/2} + \frac{1}{n} \log K_{\text{eq}} + \frac{m}{n} \log [\text{D}]_0 . \quad (\text{B})$$

Upon rearrangement of Eq. (B) the expression,

$$\text{pH}_{1/2}^0 - \text{pH}_{1/2} = \frac{1}{n} (\log K_{\text{eq}} - \log K_{\text{eq}}^0) + \frac{m}{n} \log [\text{D}]_0 ,$$

is obtained. The differences can be designated as Δ and the

above expression reduces to

$$\Delta \text{pH}_{1/2} = \frac{1}{n} (\Delta \log K_{\text{eq}}) + \frac{m}{n} \log [\text{D}]_0 . \quad (33)$$