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SOLVENT EXTRACTION OF Eu(III) INTO MIXTURES OF THENOYLTRIFLUOROACETONE WITH VARIOUS ALKYLPHOSPHINE OXIDES

by

Mark Allen Carey

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INTRODUCTION

When tri-_n_-butylphosphate (TBP) was introduced as a reagent for the solvent extraction of lanthanides and actinides, discrepancies were often found between values for distribution ratios obtained in different laboratories. The source of these differences was traced to the use of inhomogeneous material containing varying amounts of partly esterified phosphoric acid (51). These observations appear to be the first encounter with the phenomenon of synergism, although it was not recognized as such. Blake _et al_. (15) first coined the term synergism to describe the enhanced extraction of uranium(VI) from aqueous solution by a mixture of a dialkylphosphoric acid and a neutral organophosphorus compound.

The phenomenon of synergism, defined as the cooperative action of discrete agents such that the total effect is greater than the sum of the two effects taken independently, has been found in many solvent extraction systems. By far the most extensively studied systems have been the metal ion, aqueous anion/HTTA[1], neutral organophosphorus compound, organic solvent systems. The enhancement of the extraction

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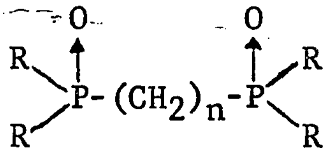
[1] See APPENDIX for structure and nomenclature.

in these systems has been explained by the formation of mixed ligand complexes of the metal in the organic phase. These mixed ligand complexes usually are adducts that the metal chelate forms with the neutral organophosphorus compound.

Although many neutral organophosphorus compounds have been used in mixed ligand solvent extraction systems, none of these have been bifunctional ligands. It was decided that an investigation of the synergic solvent extraction systems Eu(III); Cl^-, ClO_4^-, or OAc^-/HTTA; diphosphine oxide or tri-*n*-octylphosphine oxide; cyclohexane would be of interest for a variety of reasons.

The diphosphine oxides that are of interest are a series of compounds that were synthesized by members of the staff of the Ames Laboratory (Ames, Iowa). The general formula for these compounds is



$$R_2P(O)-(CH_2)_n-P(O)R_2$$

where R is the *n*-hexyl group and n has values of 1, 2, 3, and 4. These compounds were synthesized in an attempt to build specificity into a neutral organophosphorus extractant, and they have indeed been found to be useful for several separations (80). It was thought that these compounds (particularly the one with n = 1) might be able to function as bidentate ligands and form a ring with the metal. Evidence (70,71) has been found that indicates that all four of the bifunctional phosphine oxides can form complexes with uranium in which they form a ring with the metal. It was decided that a study of the adducts formed by the diphosphine oxides with $Eu(TTA)_3$, which has a limited number of unoccupied coordination sites, would shed more light on the manner in which they coordinate.

Europium(III) was selected as the metal ion for this study for several reasons. First of all, trivalent lanthanides exhibit larger synergic effects than most metal ions. Secondly, with the advent of color television europium is, perhaps, the most important of the rare earths, commercially. Most important is the very strong red fluorescence of the complex of europium with TTA which shows much potential for the fluorometric determination of europium but is difficult to utilize because HTTA extracts europium very poorly. Addition of an organophosphorus compound, however, makes the extraction very efficient and increases the fluorescent efficiency; therefore, a survey of the synergic solvent extraction of europium in a variety of systems is of interest.

Cyclohexane was chosen as the organic solvent because the largest synergic effects are observed using this solvent and because it has very good spectral qualities for fluorometric measurements.

A study of adduct formation also sheds light on the coordination capabilities of the metal studied, because the replacement of coordinated water by the neutral organophosphorus reagent makes it possible to account for all of the ligands coordinated to the metal ion.

It was with the above thoughts in mind that the investigation described in this thesis was initiated.

REVIEW OF THE LITERATURE

The work reported in this thesis is primarily concerned with synergic extractions of Eu(III) into mixtures of thenoyltrifluoroacetone[1] with neutral organophosphorus reagents. This review will, therefore, cover the literature pertinent to the study of synergic solvent extraction systems which involve a complexing acid and a neutral donor molecule.

Synergic Solvent Extraction Systems

The term synergism was first applied, in analogy to biochemical usage, to solvent extraction systems by Blake _et al_. (15). They used the term to describe the cooperative action of individual extractants which gives a larger total effect, when these reagents are used in combination, than the sum of the effects when they are used independently.[2] The first report of a large synergic effect appears, however, to have been made by Cuninghame _et al_. (23), who found that small concentrations of tributylphosphate (TBP) in the organic phase greatly enhanced the extraction of neodymium and praseodymium

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[1] See APPENDIX for structures and nomenclature.

[2] The terms synergic, synergistic, and synergetic have been used to describe this effect. In this thesis the terms synergic effect and synergism will be used.

by HTTA. These reports opened a new area of solvent extraction, which has received considerable attention since 1959.

Mixture of a dialkylphosphoric acid with a neutral organophosphorus reagent

Synergic solvent extraction with a mixture of a dialkylphosphoric acid with a neutral organophosphorus reagent has been reviewed by several authors (9,25,67,82,103); therefore, the review given here will be limited to marking important milestones in the history of synergic solvent extraction and citing information that enables the reader to compare these systems with those involving HTTA.

In 1958 Blake *et al*. (15) reported the first study of synergism in dialkylphosphoric acid-neutral organophosphorus reagent systems. The authors stated that synergic enhancement of the extraction coefficient seemed limited to dialkylphosphoric acid-neutral reagent combinations and that among the elements, Fe, U, V, Th, Al, and rare earths, only uranium extracts synergically. Synergism has since been shown to occur in many solvent extraction systems which do not involve either U(VI) or a dialkylphosphoric acid; therefore, it appears that the conclusions of Blake *et al*. (15) were too broad.

Blake et al. (16) proposed that the enhanced extraction of U(VI) occurs through the formation of an addition product in the organic phase according to the reaction

$$UO_2(A_2H)_{2(o)} + L_{(o)} \rightleftarrows UO_2(A_2H)_2L_{(o)} ,$$

where HA is a dialkylphosphoric acid, L is a neutral organophosphorus compound, and the subscript "(o)" refers to species in the organic phase. They showed that the order of synergic enhancement was $(RO)_3PO < R(RO)_2PO < R_2(RO)PO < R_3PO$ and suggested that the neutral organophosphorus compound was attached to the uranyl-dialkylphosphate complex by hydrogen bonding. It was also noted that with increasing [L] at constant $[(HA)_2]$ the extraction coefficient rose to a maximum and then decreased, and they proposed that hydrogen bonding between $(HA)_2$ and L accounts for this behavior.

Kennedy (57) postulated that the substitution reaction

$$UO_2(A_2H)_{2(o)} + 2L_{(o)} \rightleftarrows UO_2A_2L_{2(o)} + (HA)_{2(o)}$$

would be favored by the dimerization free energy of the two moles of HA liberated.

Dyrssen and Kuča (30) have concluded, after an extensive study of the U(VI), H_2SO_4/di-n-butylphosphoric acid, TBP system, that a monosubstituted product is formed by the reaction

$$UO_2(A_2H)_{2(o)} + L_{(o)} \rightleftarrows UO_2A_2(HA)L_{(o)} + HA_{(o)} ,$$

and Kennedy and Deane (58) find their infrared measurements to be consistent with this reaction. Baes (9) considers A_2H_2L to be the likely species formed by hydrogen bonding between HA and L rather than AHL, which was considered by Dyrssen and Kuča (30). After taking into account the formation of A_2H_2L in a treatment of the data of Blake *et al*. (16), Baes (9) concluded that it appears from the available extraction data that the addition product proposed by Blake *et al*. (16) is responsible for the synergic effect in dialkylphosphoric acid-neutral organophosphorus compound systems.

Mixture of thenoyltrifluoroacetone (HTTA) and a neutral donor molecule

Synergism with HTTA has been reviewed briefly by four authors (25,42,67,82). Having considered the conclusions of Blake *et al*. (15), which were described in the previous section of this review, Irving and Edgington (51,56) felt that these statements were too encompassing, since their analysis of the phenomenon of synergic enhancement of solvent extraction indicated that synergism may be realized in a number of systems provided that the following sufficient conditions were satisfied:

(i) One of the extractants should neutralize the charge on the metal ion, preferably by chelation.
(ii) The second extractant should displace any residual coordinated water from the formally neutral metal complex and render it less hydrophilic.
(iii) The second extractant should not be hydrophilic and should be less strongly coordinated than the first (chelating) extractant.
(iv) The maximum coordination number of the metal should not be exceeded.
(v) The geometry of the ligands should be favorable.

Irving and Edgington published a series of papers in which they studied the synergic extraction of a number of metals from nitric acid medium with HTTA and TBP or tri-n-butylphosphine oxide (TBPO) in cyclohexane. In the first two papers (51,56) they studied the synergic extraction of U(VI). They reported the formulae of the uranium-containing species in the organic phase to be $UO_2(TTA)_2(TBP)$, $UO_2(TTA)_2(TBPO)$, and $UO_2(TTA)_2(TBPO)_3$.

Irving and Edgington (50) later reported on the synergic extraction of Pu(VI), Pu(III), Eu(III), Np(IV), Pu(IV), and Th(IV). In three more papers they reported data on the synergic solvent extraction of trivalent plutonium, americium, and europium (54); of tetravalent thorium, neptunium, and plutonium (53); and of plutonium(VI) and neptunium(V) (52). It was reported that Np(V) extracts as $NpO_2(TTA)(HTTA)(TBP)$ and that Pu(VI) extracts as $PuO_2(TTA)_2(TBP)$. Th(IV) was reported to extract into mixtures of HTTA with TBP as a mixture of $Th(TTA)_4$, $Th(TTA)_3(NO_3)(TBP)$, and $Th(TTA)_2(NO_3)_2(TBP)_2$; and $Th(TTA)(NO_3)_3(TBPO)$ was reported to be involved in the extraction of Th(IV) into a mixture of HTTA with TBPO. They also reported that Pu(IV) and Np(IV) are extracted as a mixture of $M(TTA)_4$ and $M(TTA)_3(NO_3)(TBP)$ or as a mixture $M(TTA)_2(NO_3)_2(TBPO)_2$, $M(TTA)_3(NO_3)(TBPO)$, and $M(TTA)_4$. In the case of the trivalent elements, $M(TTA)_3(TBP)_2$ (M = Pu, Am, or Eu) or a mixture of $M(TTA)_2(NO_3)(TBPO)_2$ and $M(TTA)_3$ (M = Am or Eu) were reported to be extracted.

Shortly after Irving and Edgington began their study of synergic solvent extraction from dilute nitric acid, Healy (40,41) initiated an extensive study of the synergic extraction of divalent, trivalent, and tetravalent metal ions from dilute hydrochloric acid with HTTA in conjunction with tri-*n*-octylphosphine oxide (TOPO), triphenylphosphine oxide (TPPO), di-*n*-butyl-*n*-butylphosphonate (DBBP), tri-*n*-butylphosphate, or triphenylphosphate (TPP) in various organic solvents. Synergism was found to occur in each of the systems investigated, and the complexes in the organic phase were found to be $Ca(TTA)_2S_2$, $UO_2(TTA)_2S$, $UO_2(TTA)_2S_3$ (S = TOPO), $Pm(TTA)_3S_2$, $Tm(TTA)_3S$, $Tm(TTA)_3S_2$, $Am(TTA)_3S_2$, $Cm(TTA)_3S_2$, and $Th(TTA)_4S$, where S is one of the neutral organophosphorus compounds listed above. It was also found that the distribution ratio increases in the same order as the basicity of the neutral donor molecule. One particularly interesting aspect of this extensive study is the influence of the so-called inert diluents on the distribution ratio. The composition of the species in the organic phase was found to be independent of the "inert" diluent, but the magnitude of the distribution ratio varied over several powers of ten, depending on the organic solvent used. The distribution ratio increased in the following order: chloroform < benzene < carbon tetrachloride < hexane < cyclohexane. It was observed that this order is the reverse of the sequence of the solubility of water in the pure diluent, i.e., the higher the solubility of water in the diluent, the lower the distribution ratio.

It should be noted that in every case Healy found that simple adducts were formed, and no aqueous anions (Cl^- in this case) were found to replace TTA in the complexes. The differences between the observations of Healy and of Irving and Edgington may lie in the stronger complexing ability of the nitrate ion. Sekine and Dyrssen (95) have concluded that deviations (low) from a slope[1] equal to the valence of the

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[1] See RESULTS AND DISCUSSION for the meaning of the slopes.

metal extracted, when $[HTTA]_o$ is varied, are due to the formation of $M(TTA)_n^{N-n}$ in the aqueous phase. They have also pointed out that it should be very difficult to prove that Th^{+4} is extracted as $Th(TTA)_x(NO_3)_{4-x}S_n$ (53) without actually varying the nitrate concentration. From their data Sekine and Dyrssen (95), like Healy (40), conclude that the complexes in the organic phase are of the form $Th(TTA)_4S$.

Healy et al. (44) made an extensive study of "antisynergism" with thenoyltrifluoroacetone and concluded that "antisynergism" is connected with the water content of the organic phase and with the destruction of the anhydrous synergic species, $M(TTA)_xS_y$. The activity of the enol form of HTTA is lowered by the formation of the ketohydrate form of HTTA.[1] In the same paper the authors reported the formation of the synergic complexes $M(TTA)_3(EHA)_2$, $M(TTA)_3(MIK)_2$ (M = Am or Pm), $Th(TTA)_4(EHA)$, $Th(TTA)_4(BAA)$, and $UO_2(TTA)_2(BAA)$, where BAA, EHA, and MIK are N-n-butylacetanilide, 2-ethylhexylalcohol, and methylisobutylketone, respectively. This report adds evidence in support of Irving and Edgington's proposal (51,52) that synergism is a widespread phenomenon.

Healy and Ferraro (43) followed with a report of ultra-

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[1] See APPENDIX for structures.

violet and visible absorption spectrophotometric measurements which confirm the formulae determined previously by solvent extraction measurements for the synergic complexes of uranium (VI), thorium(IV), and neodymium(III).

In a recent series of papers, Sekine and Dyrssen (92,93, 94,95,96,97,98) have studied the solvent extraction of various metal ions from perchlorate medium into mixtures of HTTA with various neutral donors in chloroform, carbon tetrachloride, or methylisobutylketone. They have determined the formulae of the complexes in the organic phase as well as the equilibrium constants for adduct formation.[1] Formation constants for the 1:1 adducts, in those cases where the maximum complex contained two neutral donor molecules, were calculated by a curve-fitting technique.

The same authors (93) have studied the synergic solvent extraction of Cu(II) and Zn(II) into mixtures of HTTA with TBP or methylisobutylketone. They found that $Cu(TTA)_2(TBP)$ $Cu(TTA)_2(MIK)$, $Zn(TTA)_2(TBP)$, and $Zn(TTA)_2(MIK)$ are the metal-containing species in the organic phase. Irving and Edgington (55) have also studied the synergic solvent extraction of

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[1] See RESULTS AND DISCUSSION for the definition of this constant.

Cu(II) and Zn(II), along with Co(II). They employed organic phases which consisted of mixtures of HTTA with TBP or TBPO in cyclohexane and an aqueous phase buffered with hydrochloric acid and sodium acetate. They found the complexes in the organic phase to be $Cu(TTA)_2(TBP)$, $Cu(TTA)_2(TBPO)$, $Zn(TTA)_2(TBP)$, $Co(TTA)_2(TBP)$, and $Co(TTA)_2(TBP)_2$. The equilibrium constants are somewhat higher than those determined by Sekine and Dyrssen (93), but this is not surprising in view of the fact that Healy (41) has shown that cyclohexane gives much larger distribution ratios than chloroform or carbon tetrachloride do. Scruggs et al. (87) have studied the Zn(II), OAc^-/HTTA, TBP, CCl_4 synergic solvent extraction system. The adduct formation constant obtained was comparable to that reported by Sekine and Dyrssen (93). Casey et al. (19) have studied the Cu(II), ClO_4^-/HTTA, TOPO, benzene system and claim to have evidence for the formation of $Cu(TTA)_2(TOPO)_2$ in addition to the $Cu(TTA)_2(TOPO)$ complex, which has been found by many workers.

The Eu(III), ClO_4^-/HTTA, neutral donor, organic solvent synergic solvent extraction systems have been studied extensively by Sekine and Dyrssen (95,96,97,98). They (95) have studied the systems, employing TBP, MIK, and undissociated

HTTA as neutral donors. Undissociated HTTA was found to form an adduct with the formula $Eu(TTA)_3(HTTA)$, when the concentration of HTTA was greater than 0.1 M; and MIK and TBP were found to give $Eu(TTA)_3S_2$ as the europium-containing species in the organic phase with the highest ligand number. This result is in agreement with what was found earlier by Healy (40) and Irving and Edgington (54). A curve-fitting technique showed the formation of $Eu(TTA)_3S$. Sekine and Dyrssen (96) have also tested the enhancement of the extraction of Eu(III) with HTTA by several different neutral donors, and they found the order of enhancement to be TOPO $>$ TBP $>$ quinoline $>$ coumarin $>$ MIK $>$ α-napthol. In chloroform α-naphthol, coumarin, and quinoline were found to form only $Eu(TTA)_3S$, while MIK, TBP, and TOPO were found to give both $Eu(TTA)_3S$ and $Eu(TTA)_3S_2$ (S = neutral donor). In carbon tetrachloride all of the donors were found to give $Eu(TTA)_3S_2$. The same authors (98) have tested the ability of undissociated β-isopropyltropolone (HIPT), a chelating acid, to function as a neutral donor in the Eu(III), ClO_4^-/HTTA, HIPT, organic solvent synergic extraction systems. They found that HIPT forms quite strong adducts with the formulae $Eu(TTA)_3(HIPT)$ and $Eu(TTA)_3(HIPT)_2$ and that its donor strength toward $Eu(TTA)_3$, as indicated by the adduct formation constants, lies between that of quinoline and TBP.

Sekine and Dyrssen (97) extended their survey of solvent extraction with mixed ligands with a study of the M(III), ClO_4^-/HTTA, neutral donor, CCl_4 systems, where M(III) is In, Sc, La, Eu, Lu, or Am and the neutral donor is TBP, MIK, or di-n-butylsulfoxide (DBSO). $In(TTA)_3$ does not form adducts with these three donors. $Sc(TTA)_3$ adds one molecule of TBP or DBSO but forms only a weak complex with MIK. The formation constants of the $M(TTA)_3(TBP)_2$ adducts show an order of stability La > Eu $\simeq$ Lu. The formation of $Lu(TTA)_3(DBSO)_2$ is weak, and the 2:1 adduct of $Lu(TTA)_3$ with MIK does not form. The donor strength of DBSO toward these complexes seems to be very similar to that of TBP.

Guillaumont (38) has examined the synergic effect in the Pa(V), $HClO_4$/HTTA, TBP, benzene system and has found that the complex that partitions has the formula $Pa(OH)_3(TTA)_2(TBP)_2$. It was also found that in the absence of TBP the complex in the organic phase is $Pa(OH)_3(TTA)_2(HTTA)_2$, and the author proposes that synergism in this system takes place by the reaction

$$Pa(OH)_3(TTA)_2(HTTA)_{2(o)} + 2TBP_{(o)} \rightleftharpoons Pa(OH)_3(TTA)_2(TBP)_{2(o)} + 2HA_{(o)}.$$

Several authors have studied the synergic effect of amines on the extraction of metal ions with HTTA. Probably the most significant of these are the two comprehensive studies made by Newman and Klotz (76,77). In the Th(IV), Cl^-/HTTA, TOA, benzene system (TOA = tri-n-octylamine) (77), synergism was attributed to the organic phase reaction

$$Th(TTA)_4 + TOA\cdot HCl \rightleftharpoons Th(TTA)_4(TOA\cdot HCl) \ .$$

The other amine species, TOA·HCl·HTTA and TOA·HTTA, were found to give no synergic effect. It was concluded that the amine hydrochloride is attached to one of the TTA ligands rather than to the central metal atom. In the second study (76) Am(III) was substituted for Th(IV), and the synergic effect was attributed to the following organic phase reactions:

$$Am(TTA)_3 + TOA\cdot HCl \rightleftharpoons Am(TTA)_3(TOA\cdot HCl) \ ,$$

$$Am(TTA)_3 + TOA\cdot HTTA \rightleftharpoons Am(TTA)_3(TOA\cdot HTTA) \ ,$$

and $$Am(TTA)_3 + TOA\cdot HCl\cdot HTTA \rightleftharpoons Am(TTA)_3(TOA\cdot HCl\cdot HTTA) \ .$$

It was concluded that in this case the amine bonds directly to the central metal atom, on the basis that all three amine species appear to cause synergism. Takei (104) has found synergism attributable to the reaction

$$UO_2^{+2} + 2HTTA_{(o)} + TOA\cdot HClO_{4(o)} \rightleftharpoons UO_2(TTA)_2(TOA\cdot HClO_4) + 2H^+ ,$$

but, unlike Newman and Klotz, he finds no evidence for an interaction of HTTA with TOA or TOA·$HClO_4$. Synergic systems involving HTTA and amines have also been studied by Casey and Walker (20), Irving (46), and Nikolić and Gal (79).

Several practical applications of synergic solvent extraction have been made, and one of the most significant is the determination of stability constants for aqueous complexes, e.g., complexes with NO_3^-, Cl^-, SO_4^{-2}, etc. Sekine et al. (88, 89,90,91,100,101) have found the use of a mixture of HTTA with TBP or MIK very useful for the determination of aqueous phase stability constants, because the distribution ratio can be varied over a very wide range merely by changing the concentration of the adduct-forming ligand. Moreover, these systems allow the use of very low concentrations of HTTA in the organic phase; therefore, the extent of complexation of the metal by HTTA in the aqueous phase is decreased, removing one very serious complication from the system.

Separations of metals and the determination of metal ions have also been accomplished using synergic solvent extraction. Sekine and Dyrssen (95) have compiled all of the previously determined equilibrium constants for the formation of synergic complexes, and this compilation should serve as a useful guide for the exploitation of the analytical potential of synergic solvent extractions. Manning (65), in a study of the Ln^{+3}, HNO_3/HTTA , dialkylalkylphosphonate, kerosene systems (Ln^{+3} = Y^{+3}, Sc^{+3}, or trivalent lanthanides), has concluded that steric effects are dominant in these systems and that in many cases these effects lead to poor separation factors. However, in systems where the lighter lanthanides form 2:1 adducts and the heavier ones 1:1 adducts, desirable separation factors may be obtained. Awwal (8) has developed a radiochemical method for the determination of Ce(III), using synergic extraction with HTTA and TBP. The method provides a clean separation of radiocerium from other fission products. Akaiwa and Kawamoto (2) have used the extraction of Mn(II) into a mixture of HTTA with pyridine as the basis for a spectrophotometric determination of Mn in steel samples. The synergic effect in this system is attributable to the formation of $Mn(TTA)_2(pyridine)_2$. Sekine and Dyrssen (92) have shown that Ca(II) and Sr(II) can be separated, using a mixture of HTTA and TBP in carbon tetrachloride to extract these elements. Lefort (62) has shown that plutonium can be extracted from much larger quantities of uranium with a mixture of 0.02 M TBP and 0.1 M HTTA in benzene. Only one thousandth of the original uranium remains in the separated plutonium.

Taketatsu and Banks (105) have found the synergic extraction of the lanthanides with a mixture of HTTA and TOPO and subsequent spectrophotometric measurements on the organic phase to be useful for the determination of neodymium, holmium, and erbium in the presence of other metals. As little as one milligram of these elements can be determined in the presence of much larger quantities of many other metal ions.

Explanation of the phenomenon of synergism with thenoyltrifluoroacetone (HTTA)

Although a considerable amount of work has been done in attempts to elucidate the manner in which synergism occurs, the solution to this problem has not yet become completely clear.

Early in their extensive study of the synergic solvent extraction of metal ions into mixtures of HTTA with neutral donor molecules, Irving and Edgington (51) proposed the equation

$$M(TTA)_n(H_2O)_{N-2n} + xS \rightleftharpoons M(TTA)_n(H_2O)_{N-2n-x}(S)_x + xH_2O \ ,$$

where N is the maximum coordination number and S is a neutral donor molecule, as a possible mechanism for synergism with U(VI). When $2n + x = N$, the complex will be non-hydrated and coordinatively saturated; and the complex should be unable to form a higher solvate (e.g., with water) unless sites other than the central atom are available for attachment of the donor molecules. They continued by explaining that if $N > 2n$ (for a bidentate chelating extractant) a synergic effect should be possible provided that the geometry of the metal complex can accept the neutral donor molecules. If, however, $n = N/2$ no synergic enhancement would be expected on the basis of the above mechanism. Assuming that the value of N is eight for the actinide and lanthanide series, they predicted synergic enhancement of extraction with trivalent, pentavalent, and hexavalent ions of the actinides and trivalent ions of the lanthanides. They also predicted that no synergic enhancement would be observed with tetravalent actinides and lanthanides, since $n = N/2$ in such cases. However, they qualified their explanation and prediction by indicating that they did not expect all cases of synergic extraction to be explicable in the same terms.

Irving and Edgington (53) later found that the qualification they placed on their prediction was, perhaps, the most prophetic portion of their statements. They discovered that it was necessary to propose the reaction

$$\mathrm{M(TTA)}_{4(o)} + n\mathrm{H}^{+} + n\mathrm{NO}_3^{-} + n\mathrm{S}_{(o)} \rightleftharpoons \mathrm{M(TTA)}_{4-n}(\mathrm{NO}_3)_n(\mathrm{S})_{n(o)} + n\mathrm{HX}_{(o)}$$

in order to explain their data for the synergic extraction of tetravalent metals from nitric acid. They described this reaction as the displacement of one or more molecules of TTA from an already coordinatively saturated complex by one or more molecules of neutral donor with an equivalent number of nitrate ions being coordinated in order to preserve electroneutrality. It has been previously noted that Sekine and Dyrssen (95) felt that the apparent low dependence on $[HTTA]_o$ that Irving and Edgington found (53) may be in part due to the formation of aqueous complexes of Th(IV) with TTA. The present author would like to add that in many cases, particularly when the extraction of Th(IV) was being studied, the data of Irving and Edgington for the dependence on $[HTTA]_o$ were obtained at neutral donor concentrations that were equal to or less than the concentration of the metal in the organic phase. These conditions would tend to give apparent slopes that were lower than the expected value of four. It appears to this author that a reinvestigation of the synergic solvent extraction of tetravalent metal ions from nitric acid will be necessary before the value of the extraction mechanism proposed by Irving and Edgington for this system can really be determined.

Healy (40), like Irving and Edgington (51), felt that the adduct-former rendered the TTA complex of the metal in question less hydrophilic by the substitution of the neutral donor molecule for the waters of hydration. He, however, indicated that he felt that in the complexes with metals such as Pm(III) and Th(IV) the neutral donor would probably bond to the TTA rather than directly to the central metal atom, since he considered the TTA complexes of these metals to be coordinatively saturated. Ferraro and Healy (34) reported the isolation of $UO_2(TTA)_2S$, $UO_2(TTA)_2S_3$, $Th(TTA)_4S$, and $Nd(TTA)_3S_2$ (S = neutral organophosphorus compound). These stable complexes were all found to be anhydrous by both infrared and Karl Fisher measurements. These data seem to support the contention that synergic solvent extraction involves the displacement of water from hydrated chelates.

Walker and Li (107) have indicated that they feel that the increased solubility of the synergic complexes, when compared to the TTA-complexes, is an important driving force for synergic solvent extraction. Li _et_ _al_. (63) have measured approximate solubilities for $UO_2(TTA)_2(TBP)$ and $UO_2(TTA)_2(TOPO)$ in various organic solvents, and they have found that the solubility of the adduct with TOPO is significantly greater than that of the adduct with TBP. These data seem to correlate with the fact that TOPO gives a greater synergic enhancement of the extraction of uranium than TBP does.

The question of how the neutral donor is held in the mixed complex has been an important problem in synergic solvent extraction. Irving and Edgington (51,52,53,54,55) apparently have felt from the beginning that the neutral donor is coordinated to the central metal atom. Healy (40) felt that in at least some instances the neutral donor may be bonded to the TTA moiety of the complex. Ferraro and Healy (34) later concluded, on the basis that the P-O stretching frequencies in TOPO and TPPO were decreased on the formation of the synergic complex, that the neutral donors are bonded directly to the central metal atom.

Newman (75) compiled values of the equilibrium constant for adduct formation with several TTA-metal complexes and found that the value of this constant was a function of the number of neutral donor molecules but nearly independent of the metal ion involved. He reasoned that is the bond existed between the neutral donor and the metal there should be differences in the value of the equilibrium constant which reflect the differences in the metals. He concluded, therefore, that the bonding must be to the TTA part of the complex.

Batzar _et_ _al_. (11,12) have made an attempt to resolve the question of how the neutral donor is held in the complex.

They made a study of the synergic effect of TBP on the solvent extraction of U(VI) by furoyltrifluoroacetone, thenoyltrifluoroacetone, benzoyltrifluoroacetone, thenoylacetone, acetylacetone, benzoylacetone, dibenzoylmethane, and thenoyltrifluoro(methyl)acetone (HTTMA).[1] Synergism was observed in every case, and the effect seemed to be related to the functional groups on the β-diketone only insofar as the groups affected the acidity of the β-diketone. They concluded that bonding of the neutral donor to the β-diketone-metal complex does not take place at any site on the terminal groups of the β-diketone, since synergism occurred with β-diketones with a wide variety of terminal groups. In TTMA the hydrogen on the carbon between the carbonyls has been replaced by a methyl group, and synergism occurred in this case also; therefore, they concluded that the neutral donor molecule bonds directly to the uranium. The Th(IV), ClO_4^-/HTTMA, TBP system (11) was also tested for synergism, and enhancement of extraction was found to occur in this system also.

Sekine and Ono (99) had previously studied the Eu(III), ClO_4^-/β-diketone, TBP systems and had also concluded that synergism is a function only of the extent that the functional

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[1] The systematic name for this compound is 4,4,4-trifluoro-2-methyl-1-(2-thienyl)-1,3-butanedione.

groups affect the acidity of the β-diketone.

The manner in which the TTA complexes to the metal ion also has been subject to some controversy. Irving and Edgington (52) have claimed to have infrared evidence for a complex $UO_2(TTA)_2(TBPO)_3(H_2O)$ in which the TTA's are present only as monodentate ligands; however, they gave no data to support their contention. Ferraro and Healy (34) have made infrared measurements on synergic complexes both in the solid state and in solution. These authors assigned the infrared peak at about 1600 cm^{-1} to the C=O····M vibration in the metal-TTA complexes, and they interpreted the splitting of this band, upon the addition of a neutral organophosphorus compound, as an indication that some TTA carbonyl was becoming free. They concluded, on the basis of the splitting of the 1600 cm^{-1} band, that the synergic complexes contain both monodentate and bidentate TTA. However, Li et al. (63) have stated that it is their opinion that the assignment of bands in these spectra is uncertain because in some $M(TTA)_2$ complexes the band at 1600 cm^{-1} is already split. They apparently feel that the splitting is not due to the water of hydration because anhydrous $Cu(TTA)_2$ and $Zn(TTA)_2$ both show two bands in the 1600 cm^{-1} region. Halverson et al. (39) indicated that their infrared data for $Eu(TTA)_3(TOPO)_2$ can be interpreted on the basis of bidentate TTA, but they gave no data.

Synergic solvent extraction systems not involving HTTA or the combination dialkylphosphoric acid-neutral organophosphorus reagent

In recent years a large number of synergic solvent extraction systems have received attention. Although most of the chelating acids that have been studied are β-diketones, there have been several very diverse chelating acids studied, including dimethylglyoxime, 8-hydroxyquinoline, and β-isopropyltropolone. The neutral donor compounds that have been used are even more diverse and even include the bidentate ligand 1,10-phenanthroline.

Table 1 gives a survey of the synergic solvent extraction systems that have been studied, excluding those systems involving HTTA or the combination dialkylphosphoric acid-neutral organophosphorus reagent. The latter two types of systems were reviewed in detail in the previous sections of this review. It is easily seen that Irving and Edgington's (51,56) prediction that the phenomenon of synergism would be realized in a number of systems has been borne out.

Table 1. References to synergic solvent extraction systems not involving HTTA or the combination dialkylphosphoric acid-neutral organophosphorus reagent

Metal ions	Complexing acids	Neutral donors	References
Co(II)	acetylacetone	substituted pyridines	3
Co(II)	acetylacetone	pyridine	4,5,6
Co(III)	acetylacetone	TOPO	1
Fe(III)	acetylacetone	TOPO	1
Zn(II)	hexafluoroacetylacetone or trifluoroacetylacetone	TOPO	63
Zn(II)	hexafluoracetylacetone	TOPO	109
Cu(II)	acetylacetone	substituted pyridines, quinoline, or isoquinoline	20
Cu(II)	acetylacetone, hexafluoroacetylacetone, or trifluoroacetylacetone	TOPO, quinoline, or isoquinoline	19
Pt(IV)	di-_n_-butylphosphoric acid	tri-_n_-octylamine	26
U(VI)	dialkylphosphoric acids	tri-_n_-octylamine	27,28
Cu(II)	acetylacetone	4-methylpyridine	47
Cu(II)	acetylacetone	quinoline or isoquinoline	48

Table 1. (Continued)

Metal ions	Complexing acids	Neutral donors	References
Cu(II) Ni(II) Co(II) Zn(II) Cd(II) Pd(II)	trifluoroacetylacetone	isobutylamine	86
Cu(II)	dimethylglyoxime	quinoline or laurylamine	29
Cu(II)	dimethylglyoxime	aniline, di-n-butylamine, or piperidine	31
Ni(II)	diacetylbisbenzoylhydrazone	isoquinoline or 4-methylpyridine	49
Eu(III)	benzoyltrifluoroacetone	oxygen-containing and nitrogen-containing solvents	102
Zn(II)	dinonylnaphthalene sulphonic acid	TOPO, TBP, or EHA	108
Cu(II) Zn(II)	β-isopropyltropolone	TBP,MIK, β-isopropyltropolone	93
Eu(III) Th(IV)	β-isopropyltropolone	TBP, MIK, β-isopropyltropolone	95
Sc(III)	8-hydroxyquinoline	TBP, TOPO, or di-n-butyl-n-butylphosphonate	66
U(VI)	8-hydroxyquinoline	TBP or 8-hydroxyquinoline	110
Zn(II)	8-hydroxyquinoline	1,10-phenanthroline	22

Bifunctional Phosphine Oxides as Solvent Extractants for the Lanthanides

Mrochek and Banks (70,71) have studied the extraction of praseodymium, neodymium, samarium, and thulium from hydrochloric, nitric, and perchloric acid media into 0.05 M solutions of MHDPO, EHDPO, PHDPO, and BHDPO[1] in 1,2-dichlorobenzene. Data were obtained up to 7 M acid, and essentially no metal was extracted from hydrochloric acid by EHDPO, PHDPO, or BHDPO; however, the distribution ratio for Sm(III) from 7 M HCl into 0.05 M MHDPO was found to be 0.2. The extraction data for nitric acid media were very similar for all four compounds, with the largest distribution ratios occurring at 1 M nitric acid. Very distinct differences in distribution ratios were observed for the four compounds when extractions from aqueous perchloric acid were performed. The extraction by MHDPO was considerably higher than by each of the other three reagents for acid concentrations higher than 0.1 M. Above 0.1 M perchloric acid PHDPO and BHDPO extracted negligible amounts of the lanthanides. EHDPO exhibited an initial rapid decrease in extraction followed by a leveling off at a distribution ratio of 0.01 at a perchloric acid concentration

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[1] See APPENDIX for structures and nomenclature.

of 5 M. The order of the distribution ratios from 0.1 M perchloric acid was MHDPO $\simeq$ EHDPO > BHDPO > PHDPO.

Mrochek and Banks (71) have also briefly investigated the synergic enhancement of extraction in the Pr(III), ClO_4^- or NO_3^-/HTTA, MHDPO or EHDPO, 1,2-dichlorobenzene systems. The enhancement was found to be much greater in the presence of perchlorate than in the presence of nitrate. The enhancement by EHDPO was slightly greater than that by MHDPO.

O'Laughlin (80) has reviewed the extraction of the lanthanides by neutral bifunctional organophosphorus compounds, and the reader is referred to his review for information on compounds other than MHDPO, EHDPO, PHDPO, and BHDPO. O'Laughlin (80) has also reviewed the use of bifunctional neutral organophosphorus compounds (including MHDPO, EHDPO, PHDPO, and BHDPO) in the reversed-phase partition chromatography of the lanthanides.

APPARATUS AND REAGENTS

Gamma ray count rates were determined using a Radiation Instruments Development Laboratory, single channel, well-type, gamma ray, scintillation counter with a thallium-doped sodium iodide detector. Fluorometric measurements were made using an Aminco-Bowman spectrophotofluorometer in combination with a 1P-21 photomultiplier tube. Fluorescence spectra were obtained using a Moseley X-Y recorder. Spectrophotometric measurements were made with a Beckman, Model DU, quartz spectrophotometer. A Beckman, Model GS, pH meter with a glass indicator electrode and a fiber-type saturated calomel reference electrode was used for all pH measurements. When pH measurements were made on solutions containing perchlorate ions, a sodium nitrate salt bridge was placed between the calomel electrode and the solution.

Solutions of europium were prepared by dissolving in dilute acid the 99.9% pure oxide, which had been purified by ion exchange at this laboratory. The solutions were standardized by titration with EDTA using xylenol orange indicator. The tracer Eu^{152} + Eu^{154} was obtained from Oak Ridge National Laboratory. The tracer Eu^{152m} was prepared by irradiation of pure europium oxide in the Ames Laboratory Research Reactor.

Arsenazo [3-(2-arsenophenylazo)-4,5-dihydroxynaphthalene-2,7-disulfonic acid] was obtained from Eastman Organic Chemicals and was purified according to the procedure of Fritz *et al.* (36). Chlorophosphonazo III [2,7-bis(4-chloro-2-phosphonobenzeneazo)-1,8-dihydroxynaphthalene-3,6-disulphonic acid] was synthesized in this laboratory according to procedures given in the literature (32,74).

The solvents cyclohexane and 1,2-dichlorobenzene were obtained from Matheson, Coleman, and Bell and were used without further purification.

Tri-*n*-octylphosphine oxide, an Eastman Organic Chemicals product, was used without further purification. Thenoyltrifluoroacetone was obtained from Peninsular Chemresearch, recrystallized twice from hexane, and dried in a vacuum desiccator. Solutions of HTTA were prepared fresh at maximum time intervals of four days. The solutions were always stored in the dark until just before use. Methylenebis(di-*n*-hexylphosphine oxide), MHDPO, was synthesized in this laboratory by Mr. J. J. Richard. The synthesis and purification of this compound have been reported in the literature (85). Dimethylenebis(di-*n*-hexylphosphine oxide), EHDPO; trimethylenebis(di-*n*-hexylphosphine oxide), PHDPO; and tetramethylenebis(di-*n*-

hexylphosphine oxide), BHDPO, were all synthesized in this laboratory by Dr. J. E. Mrochek, using methods that have been reported in the literature (70,71).

All other reagents were analytical grade.

EXPERIMENTAL

Determination of Distribution Ratios

In those studies which involved an application of the law of mass action, the partition data for Eu(III) were obtained by equilibrating five milliliters of an organic phase, containing a known concentration of HTTA and of an organophosphorus reagent, with five milliliters of an aqueous phase, containing the tracer europium ($[Eu^{+3}]$ approximately 10^{-8} $\underline{M}$). The solutions were placed in glass-stoppered 15-milliliter centrifuge tubes and shaken for 2.5 hours (any exceptions will be noted) at room temperature ($24 \pm 2^{o}C$) on a wrist-action shaker. The tubes were centrifuged; two milliliter aliquots of each phase were placed in test tubes; and the radioactivity was measured. To prevent contamination by the upper phase during sampling of the lower phase, a gentle stream of air was blown through the pipet as it passed through the upper phase. The distribution ratio was calculated by dividing the gamma ray count rate of the organic phase by the gamma ray count rate of the aqueous phase. A minimum of 10^4 counts above background were accumulated for each sample, and when Eu^{152m} ($t_{\frac{1}{2}}$ = 9.3 hours) was used, half-life corrections were applied. Only one parameter (pH, $[HTTA]_o$, etc.) in the system was varied at a time. In order to maintain aqueous activity coefficients at a constant value, the aqueous ionic strength was always maintained at 0.1, except, of course, in those experiments in which $[ClO_4^-]$ was varied. Only dilute solutions of the ligands were used in order to maintain the activity coefficients of organic species at constant values.

In those experiments in which the method of continuous variations was employed, the experimental details were essentially the same as those for the application of the law of mass action, except the molar concentration of HTTA plus organophosphorus compound was held constant. Only the molar fraction of the components was varied.

A series of experiments in which the partition of Eu(III) was monitored as a function of the molar ratio of organophosphorus reagent to europium were performed. Ten milliliters of an aqueous phase containing 2.065×10^{-3} millimole of europium was equilibrated in a 60-milliliter separatory funnel with ten milliliters of an organic solution containing a known amount of HTTA and of an organophosphorus compound. The shaking procedure was the same as described previously. The amount of HTTA, approximately six times the amount of europium, was constant for a given experiment, but the molar ratio of organophosphorus reagent to europium was varied, each successive extraction having a higher molar ratio than the previous one. The aqueous phase was buffered at a pH of 5.5 with acetate. After separating and centrifuging the phases, the fluorescence of the organic phase at 617 mμ was measured using quartz cells, and the aqueous phase was analyzed spectrophotometrically for europium. The excitation of the fluorescence was accomplished with the apparent excitation maximum at 390 mμ. The spectrophotofluorometer was standardized before each use to a constant reading with a solution of the complex of aluminum with 2,2'-dihydroxy-1,1'-azonaphthalene-4-sulfonic acid in 95% ethanol (7). Two spectrophotometric methods were used for the analysis. If the europium content was greater than 3×10^{-4} millimole, the analysis was performed using the method of Fritz et al. (36). If the europium content was less than 3×10^{-4} millimole, the analysis was performed using a method employing chlorophosphonazo III. Five milliliters of 2×10^{-4} M chlorophosphonazo III was added to the sample to be analyzed, and the volume was adjusted to 40 milliliters with water. The pH was adjusted to one with 1:1 hydrochloric acid, and after transferring the solution to a 50-milliliter volumetric flask, the volume was adjusted to 50 milliliters with 0.1 M hydrochloric acid. The absorbance of the solution at 670 mμ was measured versus a reagent blank. The percentage of the europium extracted was calculated from the resulting analysis.

Unless stated otherwise it should be assumed that the diluent is cyclohexane in all extraction studies.

Fluorometric Molar Ratio Study

The complex $Eu(TTA)_3(H_2O)_2$ was synthesized by the method given by Melby et al. (68). The chelate was analyzed by digesting samples of it with a mixture of concentrated nitric and perchloric acids to destroy the organic matter and titrating the europium perchlorate with EDTA, using xylenol orange as the indicator. The analysis gave 17.69, 17.42, 17.62, and 17.52% europium (average = 17.56% Eu). The theoretical value for $Eu(TTA)_3(H_2O)_2$ is 17.85. Heating of a sample of the chelate in vacuo at 110°C for five hours gave a weight loss of 4.9%. The theoretical water content of $Eu(TTA)_3(H_2O)_2$ is 4.2%. It was concluded that the complex indeed was $Eu(TTA)_3(H_2O)_2$, in agreement with the results of Charles and Ohlmann (21).

Five milliliters of a 2×10^{-5} M solution of $Eu(TTA)_3(H_2O)_2$ in cyclohexane was added to each of a series of

25-milliliter volumetric flasks, and different known amounts of an organophosphorus reagent were added to each of the flasks, each successive flask containing more than the previous one. The fluorescence of each solution at 617 mμ was measured using quartz cells. The excitation of the fluorescence was accomplished with the apparent excitation maximum at 350 mμ. In a given experiment the fluorescence of each solution was measured at regular time intervals until a constant value for the fluorescence was obtained. The instrument was standardized as was previously described.

Loading Capacity Experiment

A solution of TOPO of known concentration was saturated with $Eu(TTA)_3(H_2O)_2$ which had been prepared by the procedure described in the previous section. The europium used in the preparation had been "tagged" with Eu^{152} + Eu^{154}. The amount of $Eu(TTA)_3(H_2O)_2$ taken up by the solution of TOPO was determined by comparing the radioactivity measured in the solution with that of a standard solution.

RESULTS AND DISCUSSION

Application of the Law of Mass Action to the Study of the Extraction of Europium(III) from Chloride Medium

The solvent extraction systems studied here can be described as consisting of two phases, an organic and an aqueous phase. Before contacting the two phases, the organic phase consists of the diluent, HTTA, and a neutral organophosphorus compound (L); and the aqueous phase contains Eu(III), Cl^- or ClO_4^-, H^+, OH^-, and, in most cases, Na^+. Before contacting the phases, one can reasonably expect that the simple components may undergo reactions with one another. In the organic phase it may be possible for HTTA to associate with itself and for HTTA and L to interact to form some hydrogen bonded species. In the aqueous phase the europium may complex with its aqueous counter ion (X^-), with water, and with hydroxide ion. In addition, when the phases are equilibrated with one another, a number of other reactions may occur. Finite amounts of L and HTTA will partition into the aqueous phase, followed by the ionization of HTTA to the extent allowed by its ionization constant and the concentration of hydrogen ion. The metal, which certainly is already complexed to some extent by H_2O, X^-, and OH^-, may combine with L, HTTA, and TTA^- to form complexes. Any neutral species produced may then partition into the organic phase. In the systems studied in this section, the predominant species of europium in the organic phase will be of the form $Eu(TTA)_3L_n$. In the following section, where X^- is perchlorate ion, however, the predominant complex in the organic phase will often be of the form $Eu(TTA)_{3-y}(ClO_4)_yL_n$.

Upon contacting the two phases, there will also be side reactions involving the ligands. HTTA can react with water to give the ketohydrate form, thus decreasing the concentration of the enol form, which is the active species in the complexation of metals. The neutral organophosphorus compound can associate with water or HX in the organic phase, thus decreasing the concentration of free L.

In order to evaluate the distribution data, it is necessary to write equilibrium expressions for the reactions which occur in the system. Before this can be done, however, it is necessary to assess the importance of the various reactions described above. In addition, it will be necessary to evaluate the possibility of changes in activity coefficients in both phases and of polymerization in the organic phase. Many of the foregoing side effects can be reasonably eliminated on the basis of existing data. Pukanic et al. (83) have used nmr to show that HTTA is monomeric in carbon tetrachloride at a concentration of 0.3 M and that the equilibrium constant of the reaction

$$\mathrm{HTTA}_{(o)} + \mathrm{TOPO}_{(o)} \rightleftharpoons \mathrm{HTTA{\cdot}TOPO}_{(o)}$$

is only 0.34 at 34°C. It will, therefore, be considered that HTTA does not associate at the concentrations used and that interactions between HTTA and L are unimportant in the concentration ranges employed. Sekine (88) has found values of only 0.7 and 0.2 for the overall formation constants of the 1:1 and 2:1 chloride complexes of europium(III), respectively. It, therefore, will be assumed that complexation of europium (III) by chloride is negligible. In the pH range (pH = 1 to pH = 2) used for the study of the synergic solvent extraction systems, the complexation of europium(III) by hydroxide ion will be considered negligible, and the extraction of species containing hydroxide ion will be considered insignificant. The formation of complexes of the form $\mathrm{Eu(TTA)}_i^{3-i}$ in the aqueous phase will be important but only at high values of $[\mathrm{HTTA}]_o/a_H$, where a_H is the activity of hydrogen ion measured on a pH meter. This will be shown later for the Eu(III), ClO_4^-/HTTA, TOPO system. It is unlikely that complexation of europium in the aqueous phase by the neutral organophosphorus compounds is important in view of the low solubilities of these compounds in water (81). It was found that the amount of hydrochloric acid extracted from 0.1 M HCl by 0.005 M HTTA plus 0.005 M MHDPO or 0.005 M TOPO in cyclohexane was less than 1% of the organophosphorus compound present. The amount of L complexed by hydrochloric acid is obviously negligible and not an important consideration. Because the ionic strength of the aqueous phase was maintained at 0.1, the activity coefficients of the species in the aqueous phase should be constant.

Inasmuch as most of the possible side reactions were eliminated on one basis or another and since the use of a radioactive tracer makes the amounts of the ligands consumed by complexation of the metal negligible, the only assumptions in the mathematical treatment given will be the following: 1) the amounts of L and HTTA tied up with water will be neglected; 2) there is no polymerization in the organic phase; and 3) the activity coefficients in the organic phase are constant at the low concentrations of ligands and metal used.

On the basis of the assumptions given above, the general equilibrium expressions for the extraction processes can be written. All of the equilibrium constants will be concentration constants with all of the concentrations given in molarity, except for the hydrogen ion which will be given as the activity (a_H) measured with a pH meter. The other symbols will be the same as defined earlier with [ ] denoting concentrations in the aqueous phase and $[\ ]_o$ indicating concentrations in the organic phase. Mixed equilibrium constants will be indicated by K^*, with the asterisk (*) intended to emphasize that it is a mixed constant. Constants which involve species in one phase only will be denoted with β. The superscript "o" will be used to denote constants for reactions in the organic phase.

The extraction of europium(III) when HTTA is the only extractant can be represented by the equation

$$Eu^{+3} + vHTTA_{(o)} \rightleftharpoons Eu(TTA)_3(HTTA)_{v-3(o)} + 3H^+,$$

where the subscript "(o)" denotes species in the organic phase. All other species are in the aqueous phase. The mixed equilibrium constant, defined as $K^*_{3,v-3,0}$, is represented by

$$K^*_{3,v-3,0} = \frac{[Eu(TTA)_3(HTTA)_{v-3}]_o\ a_H^3}{[Eu^{+3}][HTTA]_o^v} . \qquad (1)$$

The subscripts on the symbol given for the equilibrium constant indicate the formula of the complex formed with the zero indicating that there are no neutral organophosphorus ligands in the complex. The subscripts on the symbols for equilibrium constants in the remainder of the thesis will be given in an analogous manner. Sekine and Dyrssen (95) have shown that the formation of adducts of $Eu(TTA)_3$ with undissociated HTTA is not significant below about 0.1 M HTTA. Inasmuch as the concentrations of HTTA used in this study were below 0.1 M, the value of v in Equation 1 becomes three, and the equation now is written as

$$K^*_{3,0} = \frac{[Eu(TTA)_3]_o \, a_H^3}{[Eu^{+3}][HTTA]_o^3} \quad . \tag{2}$$

While europium(III) is partitioning between the two phases, HTTA also partitions to a significant extent between the phases, and at high concentrations of HTTA the complexation of Eu(III) in the aqueous phase by TTA^- becomes significant. The complexation is represented by the reaction

$$Eu^{+3} + iTTA^- \rightleftarrows Eu(TTA)_i^{3-i}$$

and the equilibrium constant

$$\beta_i = \frac{[Eu(TTA)_i^{3-i}]}{[Eu^{+3}][TTA^-]^i} \quad . \tag{3}$$

The concentration of dissociated HTTA in the aqueous phase, $[TTA^-]$, is determined by the relation

$$[\mathrm{HTTA}]_{o,\mathrm{initial}} = [\mathrm{HTTA}]_o + [\mathrm{HTTA}] + [\mathrm{TTA}^-]$$

which can be converted to

$$[\mathrm{TTA}^-] = \frac{[\mathrm{HTTA}]_{o,\mathrm{initial}}}{1 + a_H K_a^{-1} + a_H K_a^{-1} D_{\mathrm{HTTA}}} , \qquad (4)$$

where K_a is the acid dissociation constant of HTTA and D_{HTTA} is the distribution ratio of HTTA.

The extraction of europium(III) into a mixture of the extractants HTTA and L is described by the reaction

$$\mathrm{Eu}^{+3} + y\mathrm{X}^- + w\mathrm{HTTA}_{(o)} + n\mathrm{L}_{(o)} \rightleftarrows$$

$$\mathrm{Eu(TTA)}_{3-y}(\mathrm{HTTA})_{w-3+y}(\mathrm{X})_y\mathrm{L}_{n(o)} + (3-y)\mathrm{H}^+ .$$

The mixed equilibrium constant for this reaction, defined as $K^*_{3-y,y,w-3+y,n}$, is given by the relationship

$$K^*_{3-y,y,w-3+y,n} = \frac{[\mathrm{Eu(TTA)}_{3-y}(\mathrm{X})_y(\mathrm{HTTA})_{w-3+y}\mathrm{L}_n]_o \ a_H^{3-y}}{[\mathrm{Eu}^{+3}][\mathrm{HTTA}]_o^w[\mathrm{X}^-]^y[\mathrm{L}]_o^n} . \qquad (5)$$

The concentration of HTTA was never higher than 0.1 M; therefore, adduct formation with undissociated HTTA will not be important, and Equation 5 becomes

$$K^*_{3-y,y,n} = \frac{[\mathrm{Eu(TTA)}_{3-y}(\mathrm{X})_y\mathrm{L}_n]_o \ a_H^{3-y}}{[\mathrm{Eu}^{+3}][\mathrm{HTTA}]_o^{3-y}[\mathrm{X}^-]^y[\mathrm{L}]_o^n} . \qquad (6)$$

In those cases where y is zero, Equation 6 becomes

$$K^*_{3,n} = \frac{[\mathrm{Eu(TTA)}_3\mathrm{L}_n]_o \ a_H^3}{[\mathrm{Eu}^{+3}][\mathrm{HTTA}]_o^3[\mathrm{L}]_o^n} . \qquad (7)$$

If Equation 7 is divided by Equation 2, one obtains the adduct formation constant,

$$\frac{K^*_{3,n}}{K^*_{3,0}} = \frac{[\mathrm{Eu(TTA)_3L_n}]_o}{[\mathrm{Eu(TTA)_3}]_o[\mathrm{L}]^n_o} = \beta^o_{3,n} \;, \qquad (8)$$

which is the equilibrium constant for the organic phase reaction

$$\mathrm{Eu(TTA)_{3(o)}} + n\mathrm{L_{(o)}} \rightleftarrows \mathrm{Eu(TTA)_3L_{n(o)}} \;.$$

<u>HTTA as the only extractant</u>

It is necessary to determine the value of $K^*_{3,0}$ for use in the calculation of $\beta^o_{3,n}$.

Inasmuch as

$$D = \frac{[\mathrm{Eu(TTA)_3}]_o}{\sum_0^i [\mathrm{Eu(TTA)}_i^{3-i}]} = \frac{K^*_{3,0}[\mathrm{HTTA}]^3_o \, a_H^{-3}}{\sum_0^i \beta_i [\mathrm{TTA^-}]^i}$$

and β_0 is by definition one, it is apparent that at very low values of $[\mathrm{TTA^-}]$

$$D = K^*_{3,0}[\mathrm{HTTA}]^3_o \, a_H^{-3} \,.$$

According to Equation 4, low $[\mathrm{TTA^-}]$ will be achieved at low values of $[\mathrm{HTTA}]_o/a_H$; therefore, if a_H is held constant and $[\mathrm{HTTA}]_o$ is varied, a plot of log D versus log $[\mathrm{HTTA}]_o$ should approach a straight line with a slope of three at low values of $[\mathrm{HTTA}]_o$. $K^*_{3,0}$ can be calculated from the data in the linear region. Table 2 gives D as a function of $[HTTA]_o$.

Table 2. Data for the calculation of $K^{*}_{3,0}$[a]

$[HTTA]_o$	D	$[HTTA]_o$	D
0.0576	0.0712	0.00346	8.02×10^{-5}
0.115	0.220	0.0115	1.82×10^{-3}
0.173	0.480	0.0288	9.09×10^{-3}
0.230	0.887	0.0576	6.29×10^{-2}
		0.115	2.80×10^{-1}
		0.173	4.84×10^{-1}
		0.230	7.96×10^{-1}
Conditions:		Conditions:	
$[Cl^-] = 0.100$ M		$[ClO_4^-] = 0.0977$ M	
pH = 3.01		pH = 3.01	

[a] See the text for the value of $K^{*}_{3,0}$ and for an explanation of how it was calculated.

It was found that, considering the variance of the data, the extractions from chloride and perchlorate media were nearly identical; therefore, data were obtained at low $[HTTA]_o$, only for the system employing a perchlorate aqueous medium. It was found that the plot of log D versus log $[HTTA]_o$ did not actually achieve a slope of three within the range of the analytical method; however, three was approached very closely. Log $K^{*}_{3,0}$ was estimated to be -5.83 by extrapolating the limiting linear portion of the curve of slope three to log $[HTTA]_o = 0$, where

$$\log K^*_{3,0} = \log D - 3pH .$$

Irving and Edgington (54) have reported a value of -7.66 for $\log K^*_{3,0}$; however, their value was calculated from a single extraction under conditions that give very serious complexation of europium by TTA^- in the aqueous phase. Their value probably is much lower than the true value.

The Eu(III), Cl⁻/HTTA, TOPO system

The distribution ratio in this system is given by the relationship

$$D = \frac{[Eu(TTA)_{3-y}(Cl)_y(TOPO)_n]_o}{\sum_0^i [Eu(TTA)_i^{3-i}]} ,$$

which can be converted to

$$D = \frac{K^*_{3-y,y,n}[HTTA]_o^{3-y}[Cl^-]^y[TOPO]_o^n\ a_H^{-(3-y)}}{\sum_0^i \beta_i[TTA^-]^i} ,$$

where n is the maximum solvation number. At low values of $[HTTA]_o/a_H$, which are easily attainable in synergic solvent extraction systems, the expression for the distribution ratio becomes

$$D = K^*_{3-y,y,n}[HTTA]_o^{3-y}[Cl^-]^y[TOPO]_o^n\ a_H^{-(3-y)} . \qquad (9)$$

If all of the variables but TOPO are held constant, the equation becomes

$$D = Q[\mathrm{TOPO}]_o^n ,$$

where Q is a constant. If logarithms of this equation are taken, one obtains

$$\log D = n \log [\mathrm{TOPO}]_o + \log Q .$$

It is apparent that a plot of log D versus log $[\mathrm{TOPO}]_o$ will give a straight line of slope n, if all of the other variables are truly held constant. It is also easily seen that the values of all of the exponents in Equation 9 can be established by allowing one quantity at a time to vary, while holding all of the others constant.

Figure 1 is a plot of log D versus log $[\mathrm{TOPO}]_o$. The slope of the plot is two, indicating that n in Equation 9 is two. Figure 2 is a plot of log $(D/[\mathrm{TOPO}]_o^2)$ versus $\log[\mathrm{HTTA}]_o$. Log $(D/[\mathrm{TOPO}]_o^2)$ is plotted rather than log D in this case, because not all of the data were obtained at the same concentration of TOPO. The linear portion of the curve has a slope of three, indicating that 3-y in Equation 9 is equal to three. There are no chloride ions involved in the equilibrium, which is not surprising in view of the usual low extractability of ion association complexes involving chloride. The highest adduct apparently has the formula $\mathrm{Eu(TTA)_3(TOPO)_2}$. These

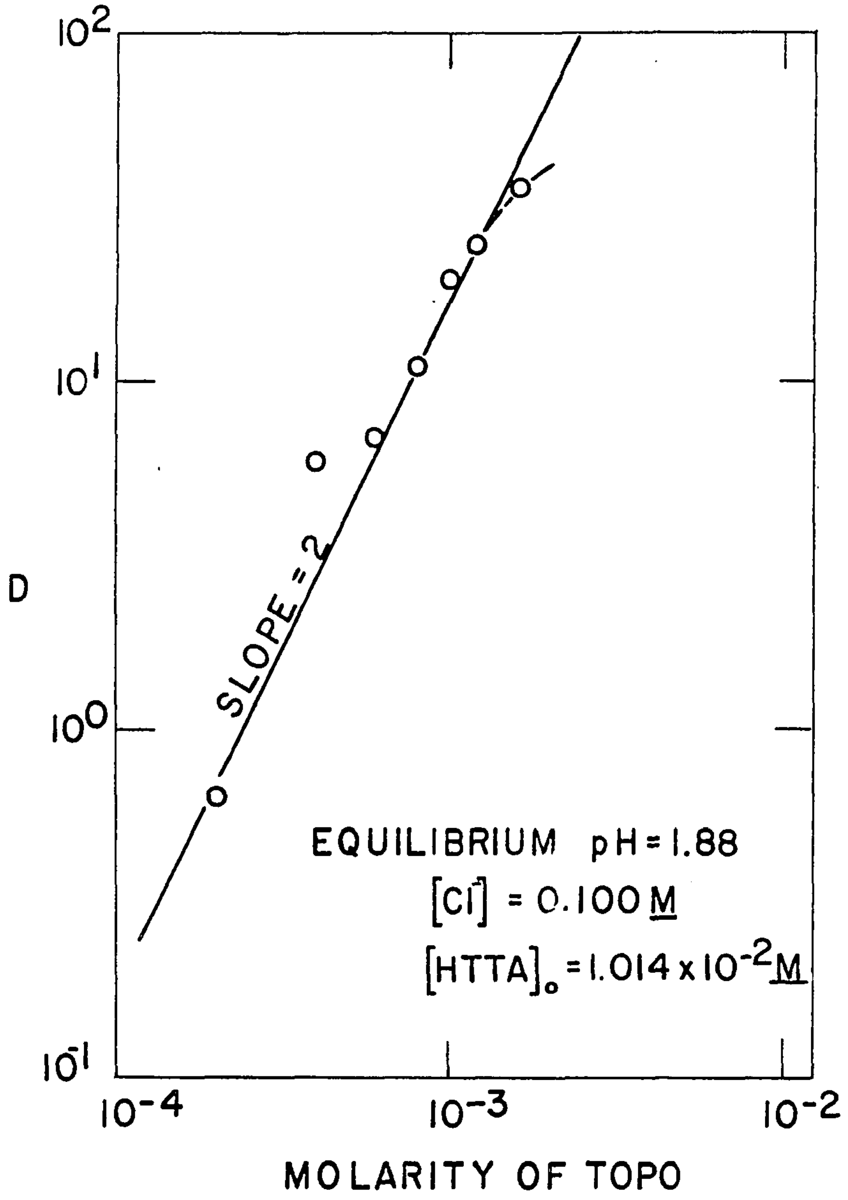

Figure 1. Dependence of the distribution ratio, D, on $[TOPO]_o$ in the Eu(III), Cl^-/HTTA, TOPO system

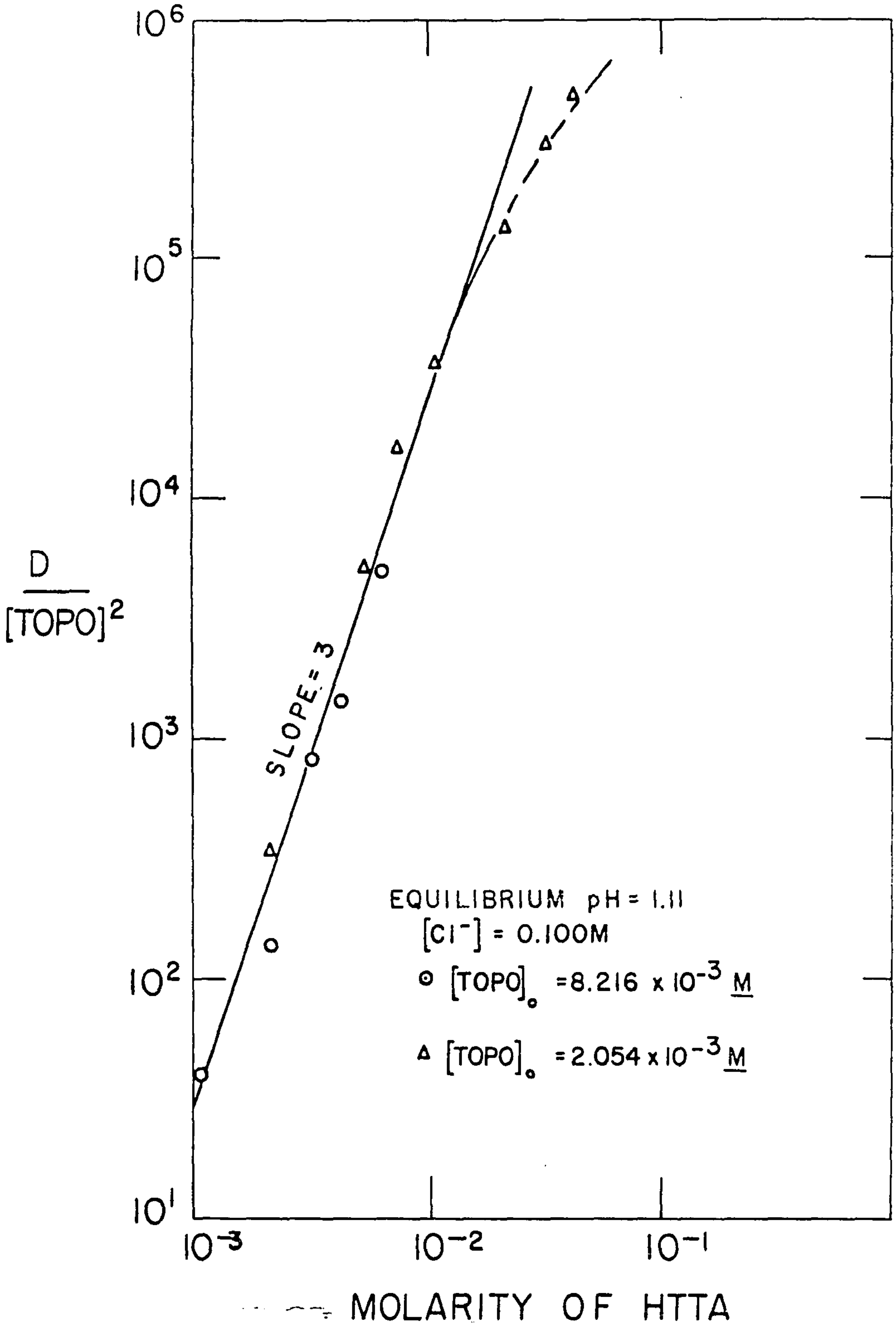

Figure 2. Dependence of the distribution ratio, D, on $[HTTA]_o$ in the Eu(III), Cl^-/HTTA, TOPO system

results are in agreement with those of Healy (40,41), who found that promethium and thulium formed $M(TTA)_3(TOPO)_2$.

Equation 7 can now be written as

$$K^*_{3,2} = \frac{D\ a_H^3}{[HTTA]_o^3[TOPO]_o^2} ,$$

and the value of $K^*_{3,2}$ can be calculated using this equation. The adduct formation constant $\beta^o_{3,2}$ is calculated by dividing $K^*_{3,2}$ by $K^*_{3,0}$ (see Equation 8). Table 3 gives the data for the linear portions of Figures 1 and 2 and also the values of $K^*_{3,2}$ and $\beta^o_{3,2}$ obtained from these data. $\mathrm{Log}(K^*_{3,2})_{ave}$ is the logarithm of the average value of $K^*_{3,2}$, and $\beta^o_{3,2}$ was calculated from this quantity. Of the values obtained for each of the constants, those ($\log K^*_{3,2} = 7.58$ and $\log \beta^o_{3,2} = 13.41$) resulting from the experiment in which $[TOPO]_o$ was varied are probably the most reliable, because the other data were obtained using concentrations of TOPO which lie in a region where deviations from linearity are observed (low D's). The slope obtained from these data remains completely valid, however. Healy (42) found values of $\log K^*_{3,2}$ of 5.0 and 5.72 for the extraction of Pm(III) and Tm(III), respectively. He also gives values of $\log \beta^o_{3,2}$ of 12.0 and 11.32 for Pm(III) and Tm(III), respectively. It is very difficult to compare actual values of data

Table 3. Equilibrium constants, $K^{*}_{3,2}$ and $\beta^{o}_{3,2}$, for the Eu^{+3}, Cl^{-}/HTTA, TOPO system

$[HTTA]_o$ ($\times 10^3$)	$[TOPO]_o$ ($\times 10^3$)	D ($\times 10^2$)	log $K^{*}_{3,2}$	$[TOPO]_o$ ($\times 10^3$)	D	log $K^{*}_{3,2}$
2.15	2.05	0.146	7.212	0.201	0.640	7.549
5.38	2.05	2.22	7.199	0.401	5.88	7.912[a]
7.54	2.05	6.66	7.238	0.602	6.91	7.629
10.8	2.05	15.2	7.127	0.802	11.1	7.586
1.08	8.22	0.270	7.170	1.00	19.6	7.641
2.15	8.22	0.942	6.816	1.20	24.8	7.585
3.23	8.22	5.53	7.053	1.60	36.1	7.498
4.31	8.22	9.66	6.920			
6.46	8.22	33.6	6.934			

log $(K^{*}_{3,2})_{ave}$ = 7.097

log $\beta^{o}_{3,2}$ = 12.93

log $(K^{*}_{3,2})_{ave}$ = 7.584

log $\beta^{o}_{3,2}$ = 13.41

Conditions: pH = 1.11

$[Cl^{-}]$ = 0.100 M

Conditions: pH = 1.88

$[HTTA]_o$ =

1.01×10^{-2} M

$[Cl^{-}]$ = 0.100 M

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[a] This value was excluded from the average.

obtained by different authors, because synergic solvent extraction systems are very sensitive to the conditions, which may not be exactly reproduced. However, it is interesting to note that Manning (65) observed that $\beta^{o}_{3,2}$ reached a maximum near the center of the lanthanide series, and this is the trend shown if one considers the data obtained here in conjunction with the data of Healy (42).

The deviation from a slope of three in Figure 2 at high $[HTTA]_o$ is probably due to the formation of $Eu(TTA)_i^{3-i}$ in the aqueous phase. This will be discussed more thoroughly in connection with the Eu(III), ClO_4^-/HTTA, TOPO system.

The rate of reaction was also studied briefly to establish the shaking time required for equilibrium. The data are given in Table 4. It was found that the distribution reached a maximum after about one-half hour and decreased until equilibrium was reached after about two hours. Apparently the extraction of europium is a rapid reaction, but the establishment of the final equilibrium in the distribution of HTTA between the organic and aqueous phases is slow. King and Reas (59) have found that HTTA is transferred rapidly to the aqueous phase, followed by a much slower establishment of distribution equilibrium. They attribute this behavior to a rapid establishment of distribution equilibrium, followed by slow establishment of the equilibrium

$$\text{enol} \rightleftarrows \text{ketohydrate}$$

in the organic phase. This explanation seems consistent with the observations made in the present work.

Table 4. Dependence of D on time in the Eu^{+3}, Cl^-/HTTA, TOPO system

Time (hours)	D
0.25	98.0
0.50	106
0.75	69.4
1.00	71.0
2.00	54.0
3.00	63.7
11.60	54.6

Conditions: $[HTTA]_o = 1.01 \times 10^{-2}$ $\underline{M}$

$[TOPO]_o = 2.01 \times 10^{-3}$ $\underline{M}$

$[ClO_4^-] = 0.0977$ $\underline{M}$

pH = 1.9

The Eu(III), Cl^-/HTTA, MHDPO system

The general equations describing the equilibria in this system are the same as those given for the previous system. The dependencies on the various parameters (a_H, $[HTTA]_o$, and $[MHDPO]_o$) were also determined in the same manner as they were for the preceding system.

Figure 3 is a plot of log D versus log $[HTTA]_o$. The slope of the linear portion of the curve is 2.7, nearly the expected value of three. The deviation from a slope of three at high $[HTTA]_o$ is probably due to the formation of $Eu(TTA)_i^{3-i}$ in the aqueous phase. This deviation will be discussed more thoroughly in connection with the Eu(III), ClO_4^-/HTTA, TOPO system. Figure 4 is a plot of log D versus log a_H. The slope of this plot is -2.9, which closely approximates three and confirms the presence of three molecules of TTA in the europium-containing species in the organic phase. Figure 5 is a plot of log D versus log $[MHDPO]_o$. The linear portion of the curve has a slope of one, indicating that the highest adduct is $Eu(TTA)_3(MHDPO)$. The formation of this complex can be described by the reaction

$$Eu^{+3} + 3HTTA_{(o)} + MHDPO_{(o)} \rightleftharpoons Eu(TTA)_3(MHDPO)_{(o)} + 3H^+ .$$

The mixed equilibrium constant for this reaction is

$$K^*_{3,1} = \frac{[Eu(TTA)_3(MHDPO)]_o \; a_H^3}{[Eu^{+3}][HTTA]_o^3[MHDPO]_o} = \frac{D \; a_H^3}{[HTTA]_o^3[MHDPO]_o} ,$$

and the adduct formation constant is given by the expression

$$\beta^o_{3,1} = \frac{[Eu(TTA)_3(MHDPO)]_o}{[Eu(TTA)_3]_o[MHDPO]_o} = \frac{K^*_{3,1}}{K^*_{3,0}} .$$

Table 5 gives the data for the linear portions of Figures 3-5

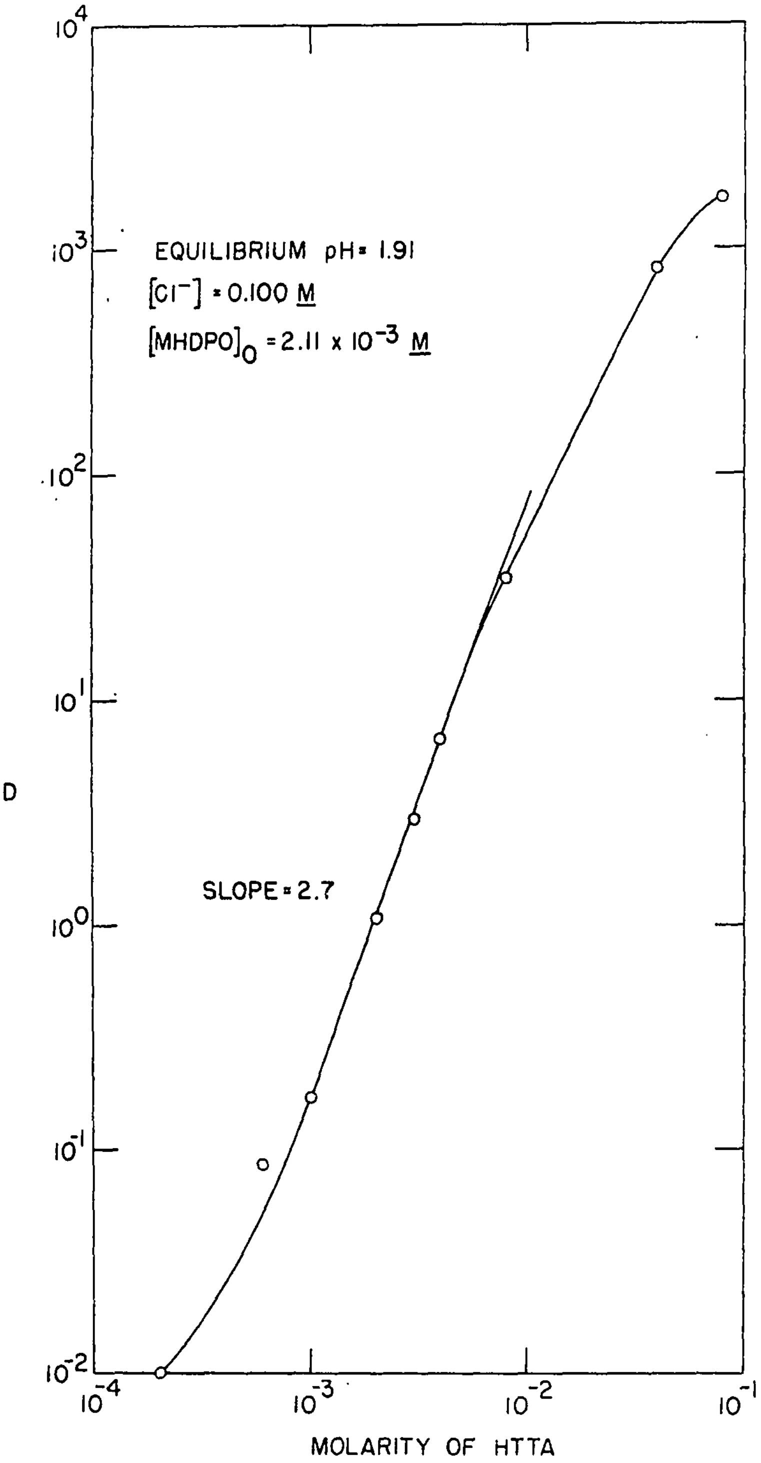


Figure 3. Dependence of the ~~distribution~~ distribution ratio, D, on $[HTTA]_o$ in the Eu(III), Cl^-/HTTA, MHDPO system

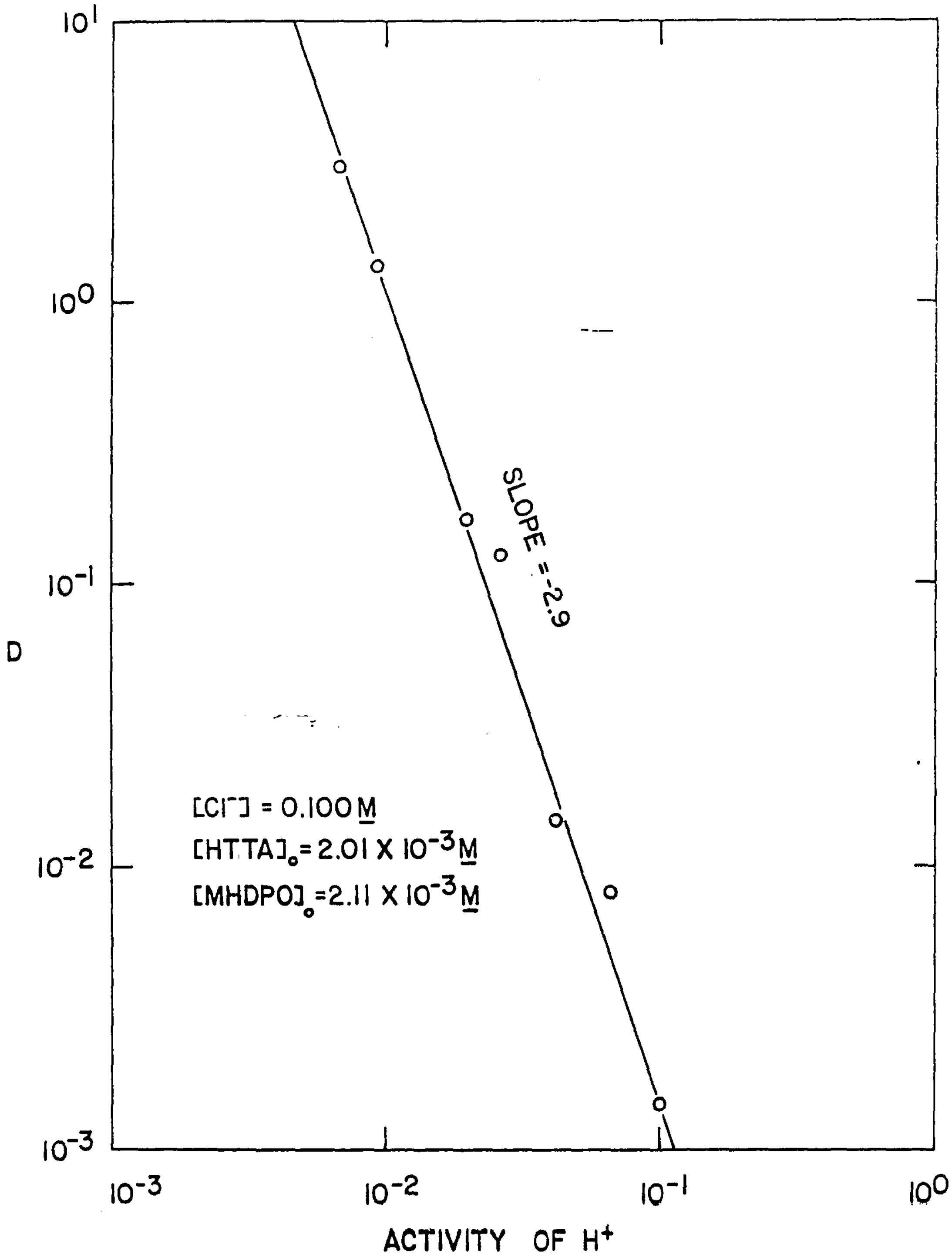


Figure 4. Dependence of the distribution ratio, D, on a_H in the Eu(III), Cl^-/HTTA, MHDPO system

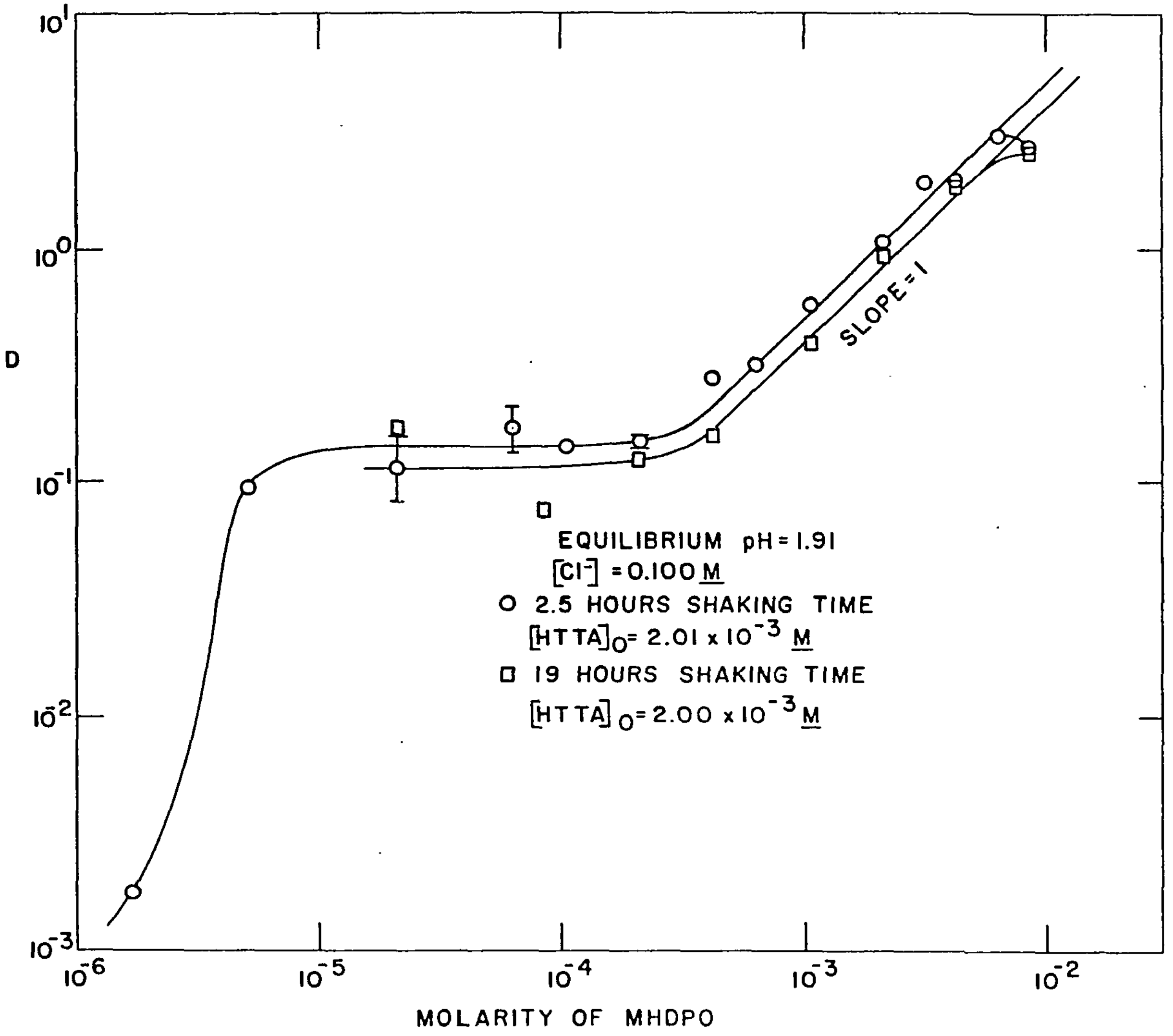


Figure 5. Dependence of the distribution ratio, D, on $[MHDPO]_o$ in the Eu(III), Cl^-/HTTA, MHDPO system

Table 5. Equilibrium constants, $K^*_{3,1}$ and $\beta^o_{3,1}$, for the Eu^{+3}, Cl^-/HTTA, MHDPO system

$[HTTA]_o$ (x 10^3)	D	log $K^*_{3,1}$	$[MHDPO]_o$ (x 10^3)	D	log $K^*_{3,1}$	a_H (x 10^3)	D (x 10^2)	log $K^*_{3,1}$
1.01	0.172	5.167[a]	0.422	0.283	5.188	100	0.145	4.927
2.01	1.09	5.072	0.634	0.316	5.057	66.8	0.809	5.149
3.02	2.96	4.977	1.06	0.574	5.093	42.2	1.47	4.810
4.02	6.77	4.963	2.11	1.05	5.057	26.6	12.5	5.137
8.05	34.8	4.769[a]	3.17	1.90	5.137	19.8	16.9	4.884
log $(K^*_{3,1})_{ave}$ = 5.009			4.22	1.91	5.017	9.33	134	4.803
			6.34	3.01	5.037	6.76	301	4.735
log $\beta^o_{3,1}$ = 10.84			log $(K^*_{3,1})_{ave}$ = 5.086			log $(K^*_{3,1})_{ave}$ = 4.948		
			log $\beta^o_{3,1}$ = 10.92			log $\beta^o_{3,1}$ = 10.78		
Conditions:			Conditions:			Conditions:		
$[MHDPO]_o$ = 2.11 x 10^{-3} M			$[HTTA]_o$ = 2.01 x 10^{-3} M			$[HTTA]_o$ = 2.01 x 10^{-3} M		
pH = 1.91			pH = 1.91			$[MHDPO]_o$ = 2.11 x 10^{-3} M		
$[Cl^-]$ = 0.100 M			$[Cl^-]$ = 0.100 M			$[Cl^-]$ = 0.100 M		

[a] These values were excluded from the average.

and the values of $K^{*}_{3,1}$ and $\beta^{o}_{3,1}$ that were calculated from these data.

The deviation from a slope of one at high $[\mathrm{MHDPO}]_o$ in Figure 5 is probably due to the so-called antisynergic effect studied by Healy et al. (44). However, the plateau between 5×10^{-6} and 3×10^{-4} $\underline{M}$ MHDPO ($D \simeq 0.15$) was unexpected. Although the distribution ratio should become constant at low $[\mathrm{MHDPO}]_o$ at a value of D equal to that given by the HTTA in the absence of MHDPO, it is obvious from the low value of $K^{*}_{3,0}$ that this value would be much lower than 0.15. It was at first thought that the fact that the points on the plateau were very difficult to reproduce might indicate that the plateau was due to the formation of some metastable species rather than an equilibrium species. This thought was tested by repeating the experiment, using a shaking time of 19 hours. It is clear from Figure 5 that equilibrium apparently had been achieved, because the curve is nearly identical to the one obtained using a shaking time of 2.5 hours. The slight displacement of the curve downward may indicate some decomposition of HTTA during the long exposure to light.

A possible explanation for the region of abnormally high distribution ratios is the formation of polynuclear species in that range of concentrations. For this to be the explanation it would be necessary for the europium-containing species in the organic phase in this region to be different from the species formed in the region of slope one. This complex would have to be capable of polymerizing and also capable of being converted at higher concentrations of MHDPO to $Eu(TTA)_3$ (MHDPO). It is felt that a complex having the formula $[Eu(TTA)_3]_2$(MHDPO) fulfills these requirements. This complex would involve two $Eu(TTA)_3$ moieties bridged by a MHDPO to form what will be called a hemisolvate. The hemisolvate would have at least one unoccupied coordination site, if, as much recent evidence seems to indicate (24,33,45,64,69), the lanthanides have maximum coordination numbers of eight to ten. Europium(III) forms many complexes in which the coordination number appears to be eight (13,61,68). The remaining coordination site in the hemisolvate could be satisfied by sharing oxygens with other molecules of the complex, forming aggregates which lead to the abnormally high distribution ratios. Filipescu et al. (35) have found by vapor pressure osmometry that anhydrous $Eu(TTA)_3$ is 45% dimeric in benzene and only 4% dimeric in chloroform. It would be expected that the extent of polymerization in the nonpolar cyclohexane would be considerably greater than in benzene.

Sekine and Dyrssen (93) have observed behavior in the Zn(II), ClO_4^-/HIPT, MIK, carbon tetrachloride system that is very similar to that observed in this work. They found a similar but less pronounced plateau in a plot of log D versus log $[MIK]_o$. They gave an explanation for this behavior that is similar to the one proposed above. They felt that $Zn(IPT)_2$ is capable of polymerizing, but the adduct with MIK, which forms at higher $[MIK]_o$, is not capable of polymerization.

Buckingham et al. (18) have found evidence in their visible absorption data for polynuclear complex formation in still another metal-mixed ligand system. They proposed that iron (II) acetylacetonate, $Fe(AA)_2$, which they believed to be monomeric, forms polymeric species upon adduct formation with pyridine (py) and that the polymerization occurs by sharing the oxygens of the acetylacetone between iron atoms. They proposed the following reactions:

$$2Fe(AA)_2 + py \rightleftharpoons [Fe(AA)_2]_2py \ ,$$

$$[Fe(AA)_2]_2py + py \rightleftharpoons [Fe(AA)_2]_2py_2 \ , \text{ and}$$

$$[Fe(AA)_2]_2py_2 + 2py \rightleftharpoons 2Fe(AA)_2py_2 \ .$$

Bertrand et al. (14) have also given evidence for a polymeric adduct. They presented vapor pressure osmometry data and visible absorption data that indicate the formation of $[Co(AA)_2]_2$ (cyclohexylamine)$_2$.

The Eu(III), Cl$^-$/HTTA, PHDPO system

A plot of log D versus log $[PHDPO]_o$ is presented in Figure 6. The slope of the linear portion of the curve is 1.1, indicating that the complex in the organic phase is probably $Eu(TTA)_3(PHDPO)$. The data for the linear segment of the curve are given in Table 6. The same table also gives

Table 6. Equilibrium constants, $K^*_{3,1}$ and $\beta^o_{3,1}$, for the Eu^{+3}, Cl^-/HTTA, PHDPO and Eu^{+3}, Cl^-/HTTA, BHDPO systems

$[PHDPO]_o$ (x 10^4)	D (x 10)	log $K^*_{3,1}$	$[BHDPO]_o$ (x 10^5)	D (x 10)	log $K^*_{3,1}$
0.548	0.388	5.217	0.302	0.131	6.004
1.10	0.844	5.250	0.756	0.291	5.952
1.37	1.15	5.290	1.51	0.559	5.935
4.11	3.94	5.348	3.02	1.08	5.920
13.7	16.4	5.444	6.05	1.69	5.813
log $(K^*_{3,1})_{ave}$ = 5.318			15.1	5.43	5.922
			30.2	9.37	5.858
log $\beta^o_{3,1}$ = 11.15			75.6	24.3	5.874
				log $(K^*_{3,1})_{ave}$ = 5.913	
				log $\beta^o_{3,1}$ = 11.74	
Conditions: $[HTTA]_o$ = 2.00×10^{-3} M			Conditions: [HTTA] = 2.00×10^{-3} M		
pH = 1.91			pH = 1.91		
$[Cl^-]$ = 0.100 M			$[Cl^-]$ = 0.100 M		

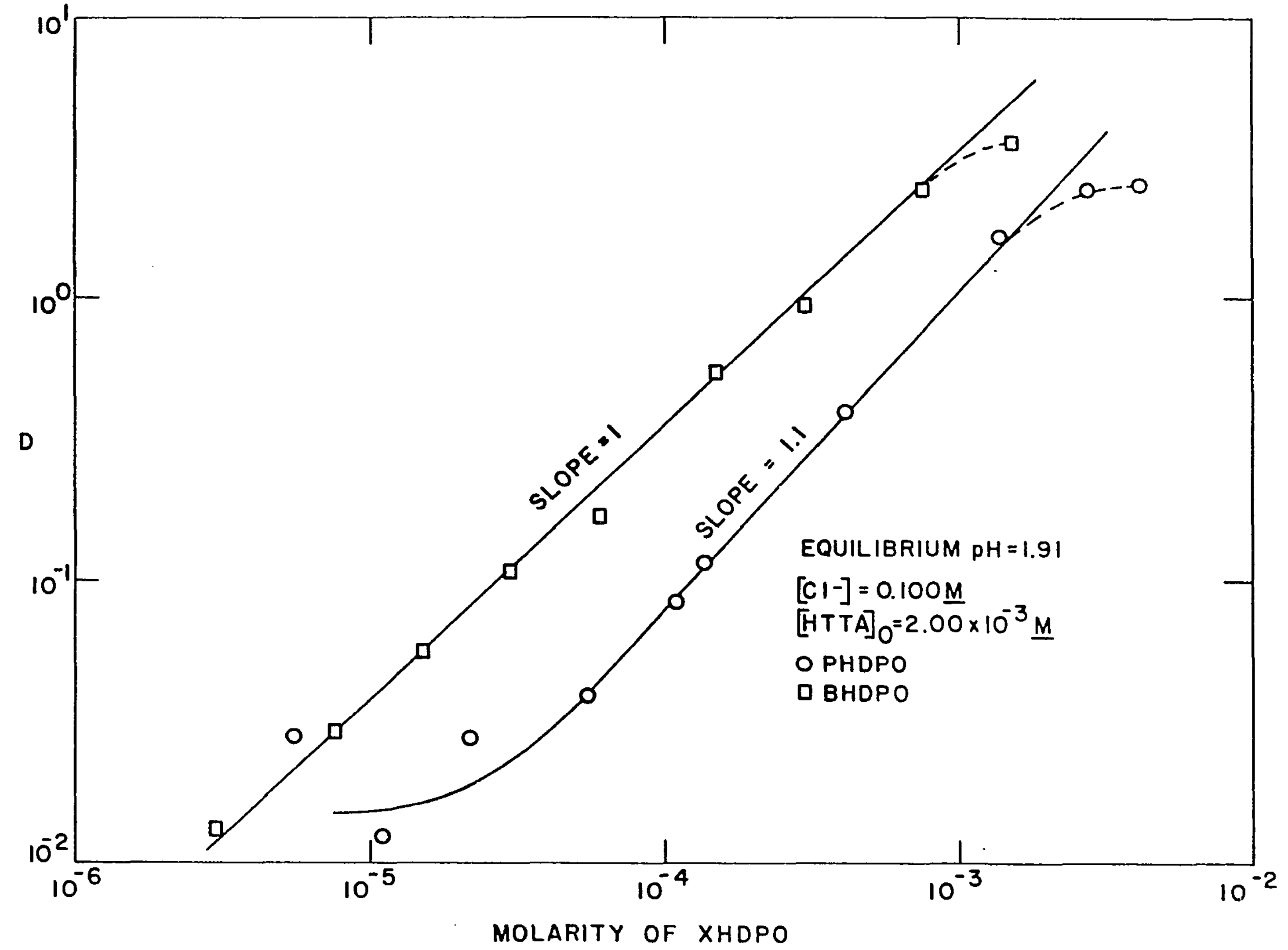


Figure 6. Dependence of the distribution ratio, D, on $[PHDPO]_o$ or $[BHDPO]_o$ in the Eu(III), Cl^-/HTTA, PHDPO or BHDPO systems

the values of $K^{*}_{3,1}$ and $\beta^{o}_{3,1}$ obtained from these data. The deviation from linearity, when the concentration of PHDPO is greater than about 2 x 10^{-3} $\underline{M}$, is probably due to the so-called antisynergic effect (44), which was also observed in the previous systems. It should be noted that this system shows a plateau below 4 x 10^{-5} $\underline{M}$ PHDPO and that the data show very poor precision in this region. The plateau occurs at a value of D which is nearly an order of magnitude lower than was observed in the Eu(III), Cl^{-}/HTTA, MHDPO system; and, likewise, the concentration of PHDPO at which the leveling off first occurs is nearly an order of magnitude lower. The explanation for this phenomenon that was applied to the previous system can probably be applied here also.

The Eu(III), Cl^{-}/HTTA, BHDPO system

Figure 6 shows a plot of log D versus log $[BHDPO]_o$ with a linear segment having a slope of one. The complex in the organic phase, therefore, has the formula $Eu(TTA)_3(BHDPO)$. The values of $K^{*}_{3,1}$ and $\beta^{o}_{3,1}$ are given in Table 6, along with the data for the linear portion of the curve in Figure 6. The deviation from linearity at about 8 x 10^{-4} $\underline{M}$ BHDPO is explained by the so-called antisynergic effect (44).

Comparison of the systems involving MHDPO, PHDPO, or BHDPO

Bauer et al. (13) have found the fluorescent spectrum of Eu(TTA)$_3$(1,10-phenanthroline) to be consistent with a C_2 symmetry about the europium ion. They also found the fluorescent spectrum of tris(4,4,4-trifluoro-1-phenyl-1,3-butanediono)(1,10-phenanthroline)europium(III) to be consistent with a symmetry of C_{2v}. Kreher et al. (61) have found the fluorescent spectra of the 1,10-phenanthroline and 2,2'-bipyridyl adducts of tris(dibenzoylmethanato)europium(III) to be consistent with a C_{2v} symmetry. Brecher et al. (17), as well as Kreher et al. (61), have indicated that an eight coordinate complex with the symmetries given above would have a spatial configuration of the coordinating atoms that would correspond to what they call a face-centered isosceles trigonal prism. The face-centered atoms are apparently centered above the two equivalent rectangular faces of the prism. If this is indeed the structure of the 1,10-phenanthroline and 2,2'-bipyridyl adducts mentioned above, it is conceivable that Eu(TTA)$_3$(MHDPO) could have a very similar structure. It is likely that PHDPO and BHDPO, due to their longer bridges between the phosphoryl groups, coordinate to the central europium ion in a different manner than MHDPO does.

It is significant to note that log $K^*_{3,1}$ increases with increasing length of the bridge between the phosphoryl groups (log $K^{*}_{3,1}$ = 5.02, 5.32, and 5.91 for MHDPO, PHDPO, and BHDPO, respectively), and, of course, log $\beta^{o}_{3,1}$ increases in the same order (10.85, 11.15, and 11.74). This order is the one that would be expected, because the basicity of the phosphoryl groups should increase in the same order.

Table 7 gives data for the extraction of water into 0.1M solutions of the phosphine oxides in carbon tetrachloride.

Table 7. Correlation of organic phase water content with antisynergism

Antisynergic deviation first occurred at	Ratio: $[H_2O]_o$/[organophosphorus compound]$_o$[a]
6.0 x 10^{-3} M MHDPO	0.77
1.5 x 10^{-3} M PHDPO	1.95
8.0 x 10^{-4} M BHDPO	2.25

[a] 0.1 M solutions in carbon tetrachloride.

These data were gathered by Mrochek et al. (73). The table also shows the phosphine oxide concentrations at which so-called antisynergic deviations from integral slopes were first observed. It is clear that the deviations occur at a lower concentration of organophosphorus reagent as the bridge between the phosphoryl groups increases in length, which is the same order as the increasing water content of the organic phase. These observations are in agreement with the findings of Healy et al. (44). They observed that so-called antisynergism is connected with the water content of the organic phase and with the destruction of the anhydrous synergic species, $M(TTA)_xL_y$.

The polymerization effect observed for the systems involving MHDPO and PHDPO was found to have its upper limit, highest concentration at which it occurs, at a lower concentration of organophosphorus reagent in the case of PHDPO. The effect was not observed for BHDPO in the range of concentrations studied, but this does not preclude the possibility that the phenomenon could be observed at even lower concentrations than it was with PHDPO. The trend BHDPO $<$ PHDPO $<$ MHDPO, shown by the upper limit of the polymerization, is probably a result of the increase in the stability of the 1:1 adduct in the order MHDPO $<$ PHDPO $<$ BHDPO.

The Synergic Solvent Extraction of Europium from Perchlorate Medium

The general equilibrium expressions given in Equations 2,3,4,6,7 and 8 for the systems in the previous section are applicable to the systems in this section also.

The Eu(III), ClO_4^-/HTTA, TOPO system

The dependencies on the various parameters (a_H, $[HTTA]_o$, and $[TOPO]_o$) were determined in the same manner as they were for the previous systems. Figure 7 is a plot of log D versus log $[TOPO]_o$. The slope is 2.0, indicating that the complex in the organic phase contains two TOPO molecules. Figure 8 is a plot of log D versus log $[HTTA]_o$, and Figure 9 is a plot of log D versus log a_H. The slope of the linear portion of the plot in Figure 8 is 2.7, and the slope of the plot in Figure 9 is -3.0. These results indicate that the complex in the organic phase is $Eu(TTA)_3(TOPO)_2$, agreeing with what was observed for the Eu(III), Cl^-/HTTA, TOPO system. Table 8 gives the data for the linear portions of Figures 7-9 and the values obtained from these data for $K_{3,2}^*$ and $\beta_{3,2}^o$. The values (log $K_{3,2}^* = 8.11$ and log $\beta_{3,2}^o = 13.94$) of the constants that were calculated from the experiment in which $[HTTA]_o$ was varied are probably the most accurate values. The other values were obtained using concentrations of HTTA at which deviations (low) from a slope of three are observed (see Table 8 and Figure 8); therefore, one would expect these values to be low. The slopes that were obtained from these data are completely valid, however. Sekine and Dyrssen (96) have found values of

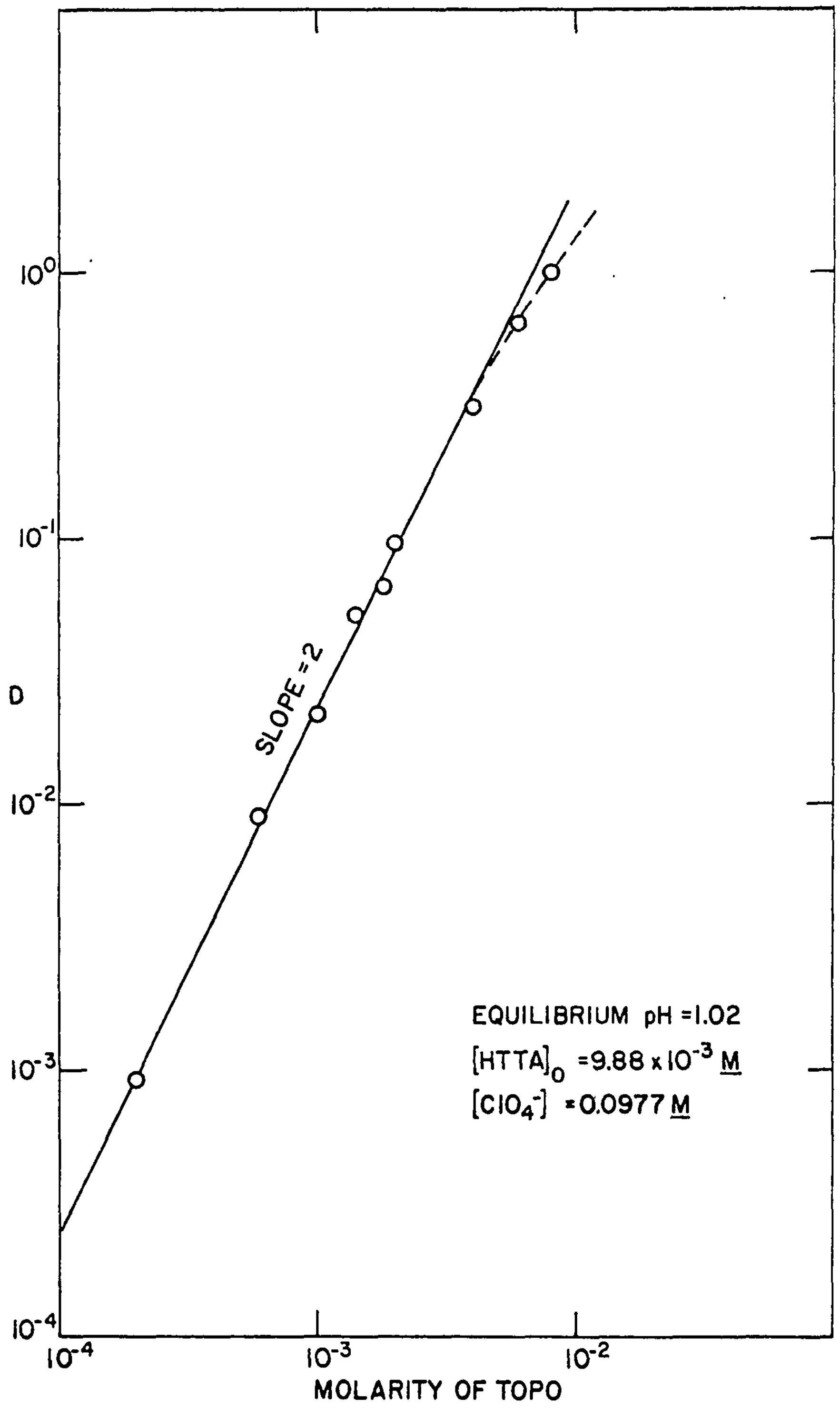


Figure 7. Dependence of the distribution ratio, D, on $[TOPO]_o$ in the Eu(III), ClO_4^-/HTTA, TOPO system

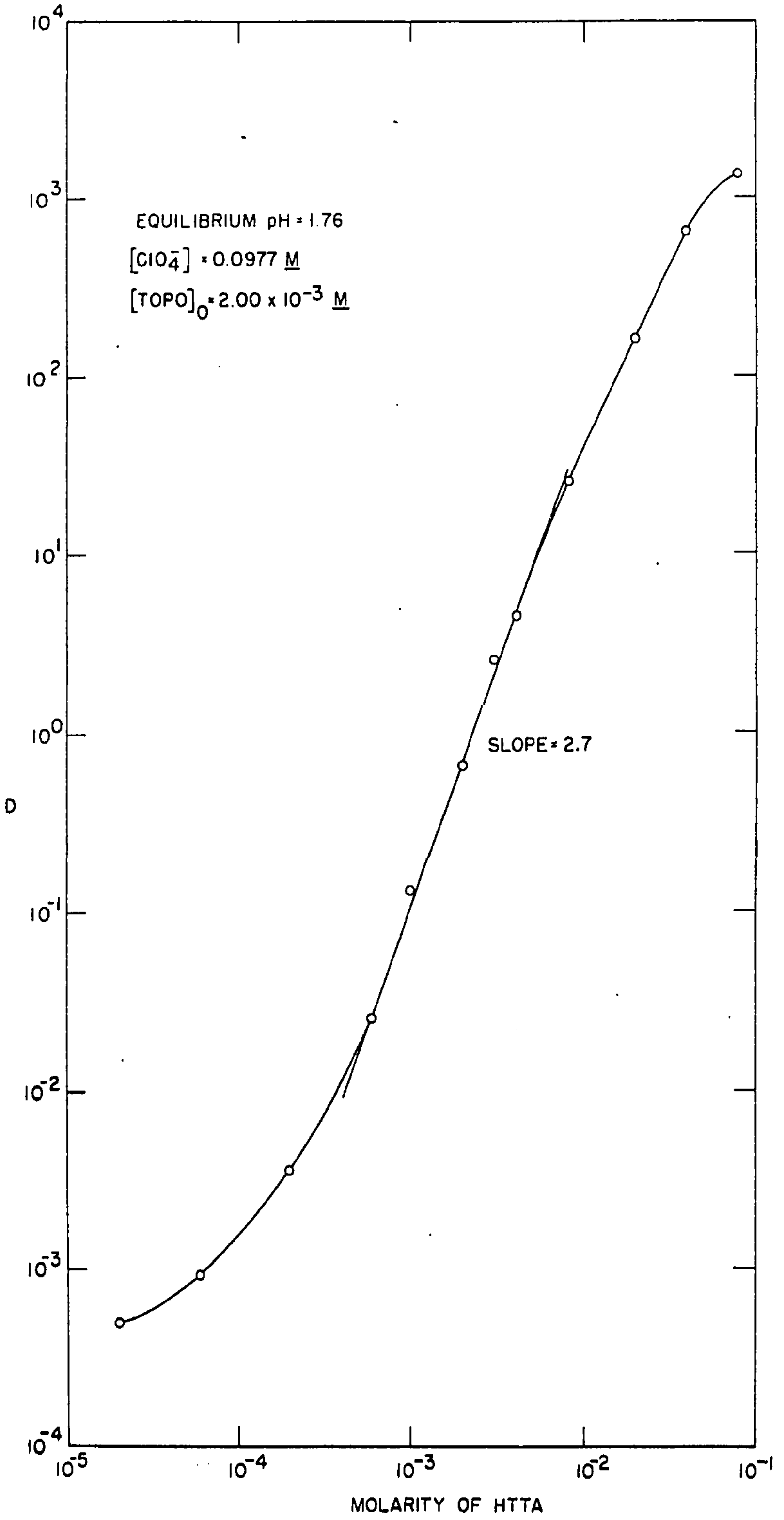


Figure 8. Dependence of the distribution ratio, D, on $[HTTA]_o$ in the Eu(III), ClO_4^-/HTTA, TOPO system

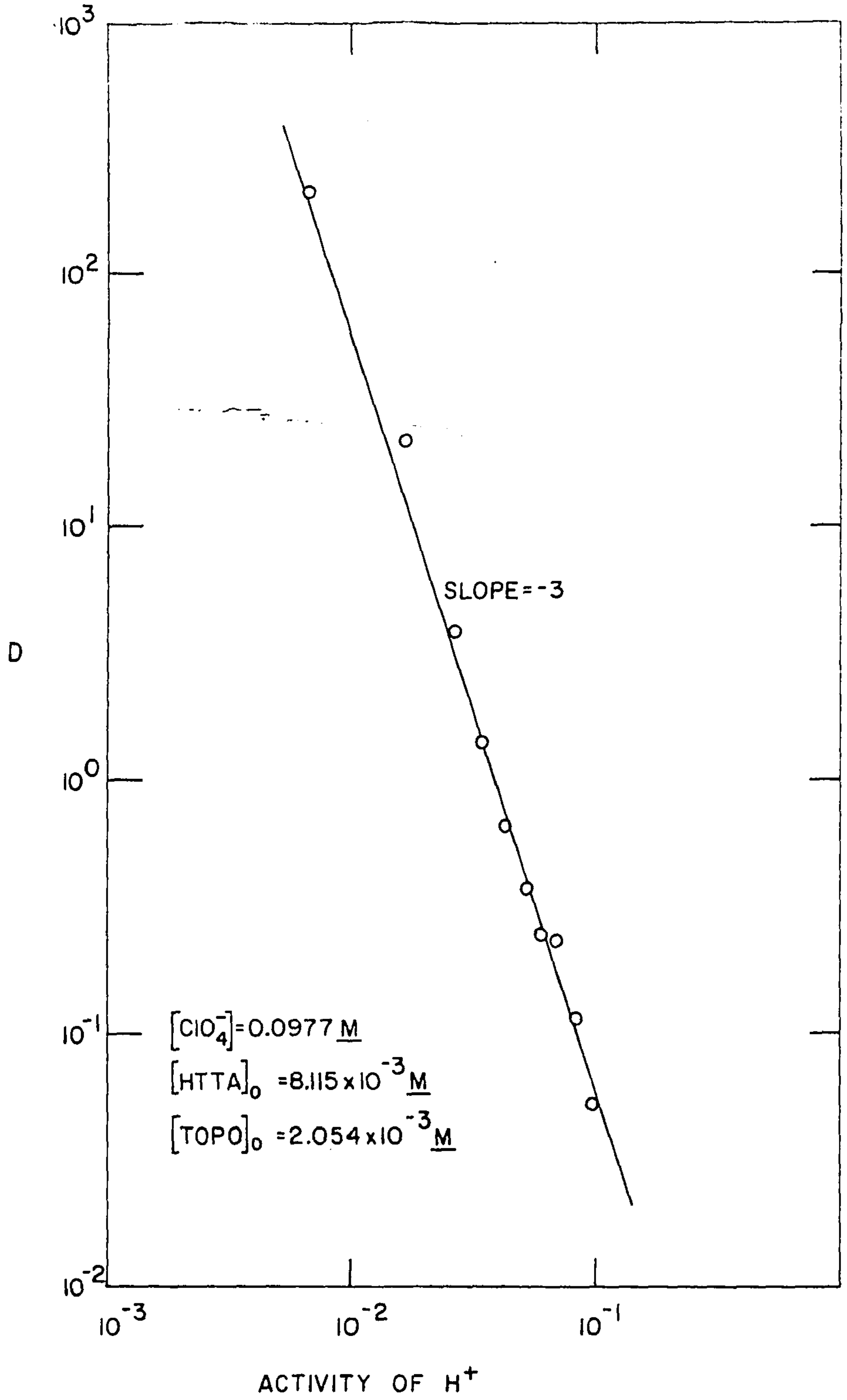


Figure 9. Dependence of the distribution ratio, D, on a_H in the Eu(III), ClO_4^-/HTTA, TOPO system

Table 8. Equilibrium constants, $K^*_{3,2}$ and $\beta^o_{3,2}$, for the Eu^{+3}, ClO_4^-/HTTA, TOPO system

$[HTTA]_o$ ($\times 10^3$)	D ($\times 10$)	log $K^*_{3,2}$	$[TOPO]_o$ ($\times 10^3$)	D ($\times 10^3$)	log $K^*_{3,2}$	a_H ($\times 10^2$)	D	log $K^*_{3,2}$
0.604	0.257	8.188	0.199	0.908	7.316	0.676	208	7.456
1.01	1.32	8.228	0.598	8.91	7.352	1.58	21.8	7.582
2.02	6.55	8.021	0.997	21.2	7.286	2.57	3.82	7.461
3.02	25.7	8.090	1.40	50.8	7.369	3.46	1.43	7.420
4.02	45.2	7.962	1.80	64.6	7.255	4.26	0.668	7.362
8.05	253	7.805[a]	1.99	94.6	7.334	5.24	0.381	7.387
log $(K^*_{3,2})_{ave}$ = 8.110			3.99	304	7.238	6.02	0.249	7.382
			log $(K^*_{3,2})_{ave}$ = 7.310			8.31	0.116	7.471
log $\beta^o_{3,2}$ = 13.94						9.76	0.053	7.340
			log $\beta^o_{3,2}$ = 13.14			6.92	0.234	7.536
						log $(K^*_{3,2})_{ave}$=7.446		
						log $\beta^o_{3,2}$ = 13.28		
Conditions:			Conditions:			Conditions:		
$[TOPO]_o$ = 2.00 x 10^{-3} M			$[HTTA]_o$ = 9.88 x 10^{-3} M			$[HTTA]_o$ = 8.12 x 10^{-3} M		
pH = 1.76			pH = 1.02			$[TOPO]_o$ = 2.05 x 10^{-3} M		
$[ClO_4^-]$ = 0.0977 M			$[ClO_4^-]$ = 0.0977 M			$[ClO_4^-]$ = 0.0977 M		

[a] This value was excluded from the average.

7.60 and 12.26 for log $\beta^{o}_{3,2}$ using chloroform and carbon tetrachloride, respectively, as solvents. The values of these constants, along with the one determined here using cyclohexane, are in the same order (cyclohexane > carbon tetrachloride > chloroform) as Healy (41) found for the synergic enhancement of the extraction of Pm(III) into these inert diluents.

The deviation from a slope of 2 at high $[\mathrm{TOPO}]_o$ is probably an "antisynergic" deviation. The causes of this deviation have been discussed earlier. The deviation from a slope of 3 at high $[\mathrm{HTTA}]_o$ in Figure 8 is probably due to the formation of aqueous complexes of the form $\mathrm{Eu(TTA)}_i^{3-i}$. The formation constants for these complexes were defined in Equation 3. The distribution ratio in this region is given by the relationship

$$D = \frac{K^{*}_{3,2}[\mathrm{HTTA}]^3_o[\mathrm{TOPO}]^2_o\ a_H^{-3}}{\sum_{0}^{i} \beta_i[\mathrm{TTA}^-]^i} .$$

Upon taking logarithms of the above expression and rearranging, one obtains

$$\log \frac{D\ a_H^3}{[\mathrm{HTTA}]^3_o[\mathrm{TOPO}]^2_o} = -\log \sum_{0}^{i} \beta_i[\mathrm{TTA}^-]^i + \log K^{*}_{3,2} , \qquad (10)$$

where $[\mathrm{TTA}^-]$ is determined with Equation 4. Reid and Calvin

(84) gave a value of 6.23 for the pK_a, and log D_{HTTA} was found by the author to be 1.1 at a pH of 1.76, the pH at which the data for Figure 8 were gathered. Upon substituting these values into Equation 4, one obtains

$$[TTA^-] = \frac{[HTTA]_{o,\ initial}}{4.02 \times 10^5} .$$

Figure 10 is a plot of log $(D\ a_H/[HTTA]_o^3[TOPO]_o^2)$ versus log $[TTA^-]$. It is apparent from Equation 10 that the plot should approach log $K^*_{3,2}$ as a horizontal asymptote at very low values of $[TTA^-]$. If β_1 is large enough and β_2/β_1 is not too great, the slope should achieve a value of minus one for a limited range and then become more negative. The curve in Figure 10 exhibits this behavior; therefore, it seems likely that the dominant effect causing the deviations shown in log D versus log $[HTTA]_o$ at high $[HTTA]_o$ is the formation of complexes in the aqueous phase. It should be pointed out, however, that this behavior is merely indicative of aqueous complexation and not proof. The above treatment was given because no values for β_i are available. To prove the proposal, it would be necessary to determine the values of the aqueous formation constants and use them to calculate the curve in Figure 10.

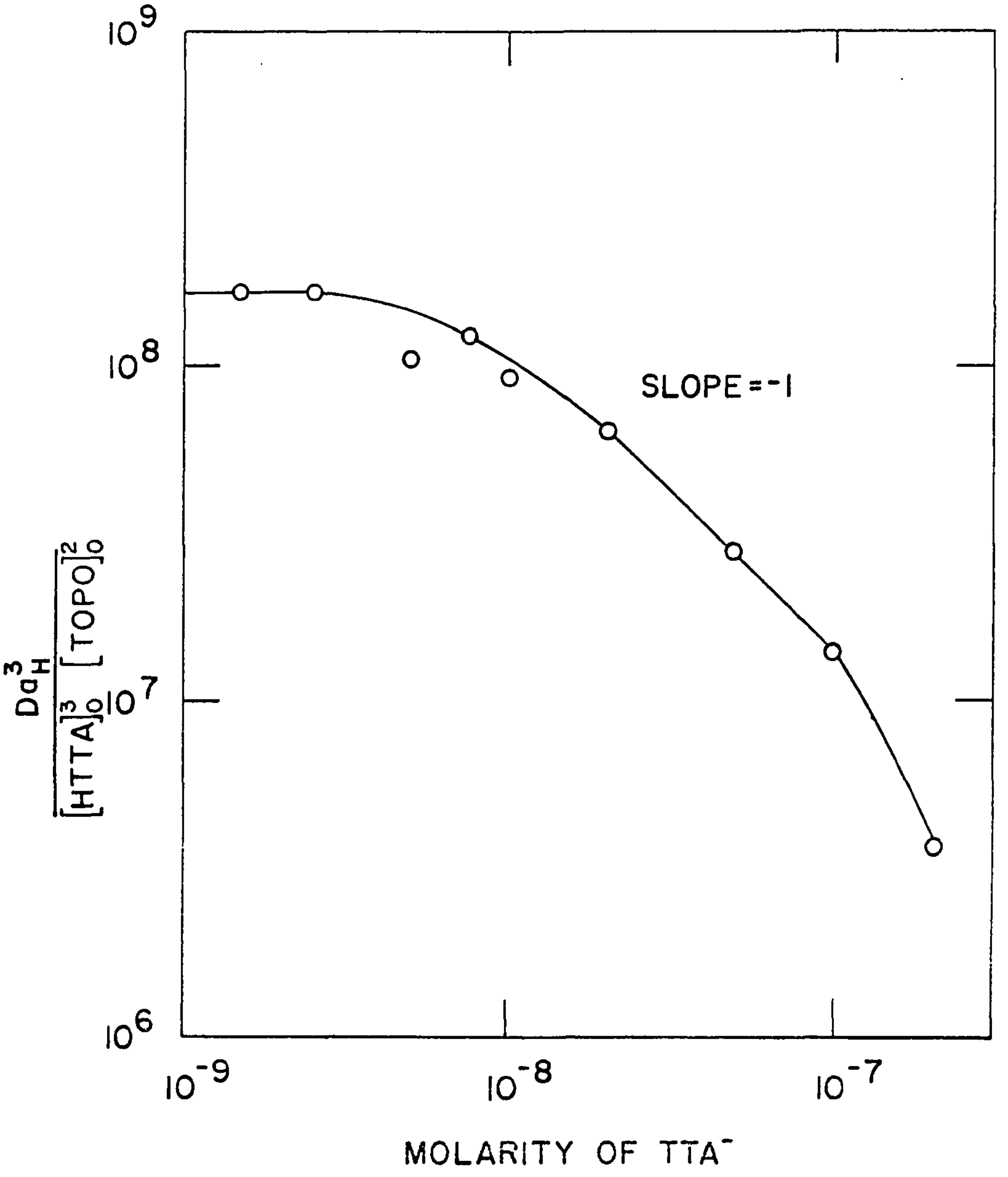


Figure 10. Change in the apparent value of $K_{3,2}^*$ with $[TTA^-]$ in the Eu(III), ClO_4^-/HTTA, TOPO system

The rate of reaction was studied briefly for this system to establish the shaking time required to establish equilibrium. The data are given in Table 9. The analysis of these data results in the same conclusions as were drawn for the Eu(III), Cl^-/HTTA, TOPO system.

Table 9. Dependence of D on time in the Eu^{+3}, ClO_4^-/HTTA, TOPO system

Time (hours)	D
0.5	0.132
1.0	0.106
1.5	0.0798
3.0	0.0816
6.0	0.0797

Conditions: $[HTTA]_o = 9.88 \times 10^{-3}$ M

$[TOPO]_o = 1.99 \times 10^{-3}$ M

$[ClO_4^-] = 0.0977$ M

pH = 1

The Eu(III), ClO_4^-/HTTA, MHDPO system

The stoichiometry of the complex formed when europium (III) is extracted from perchlorate medium into mixtures of HTTA and MHDPO in cyclohexane has been determined by application of the law of mass action. An equilibrium constant for the formation of this complex has been calculated.

The dependencies on the variables (a_H, $[\mathrm{HTTA}]_o$, etc.) were determined in the same manner as they were in the previous systems. Figure 11 is a plot of log D versus log $[\mathrm{MHDPO}]_o$. The slope of this plot is three, indicating that three MHDPO molecules are included in the complex in the organic phase. Table 10 gives data for the extraction of

Table 10. Extraction of Eu^{+3} from perchlorate medium with MHDPO

$[\mathrm{MHDPO}]_o$ (x 10^3)	D (x 10^2)
0.102	0.511
0.511	2.20
1.02	335

Conditions: pH = 1.17

$[\mathrm{ClO_4^-}] = 0.0977\ \underline{M}$

Eu(III) from perchlorate medium into solutions of MHDPO in cyclohexane. A plot of log D versus log $[\mathrm{MHDPO}]_o$ is nearly linear (slightly concave upward) and has a slope of about three. Correction of the plot in Figure 11 for the Eu(III) extracted by MHDPO in the absence of HTTA does not change the slope but shifts the curve downward slightly. Figure 12A is a plot of log D versus log a_H. The slope obtained by a least squares treatment of the data is -0.93, indicating that one

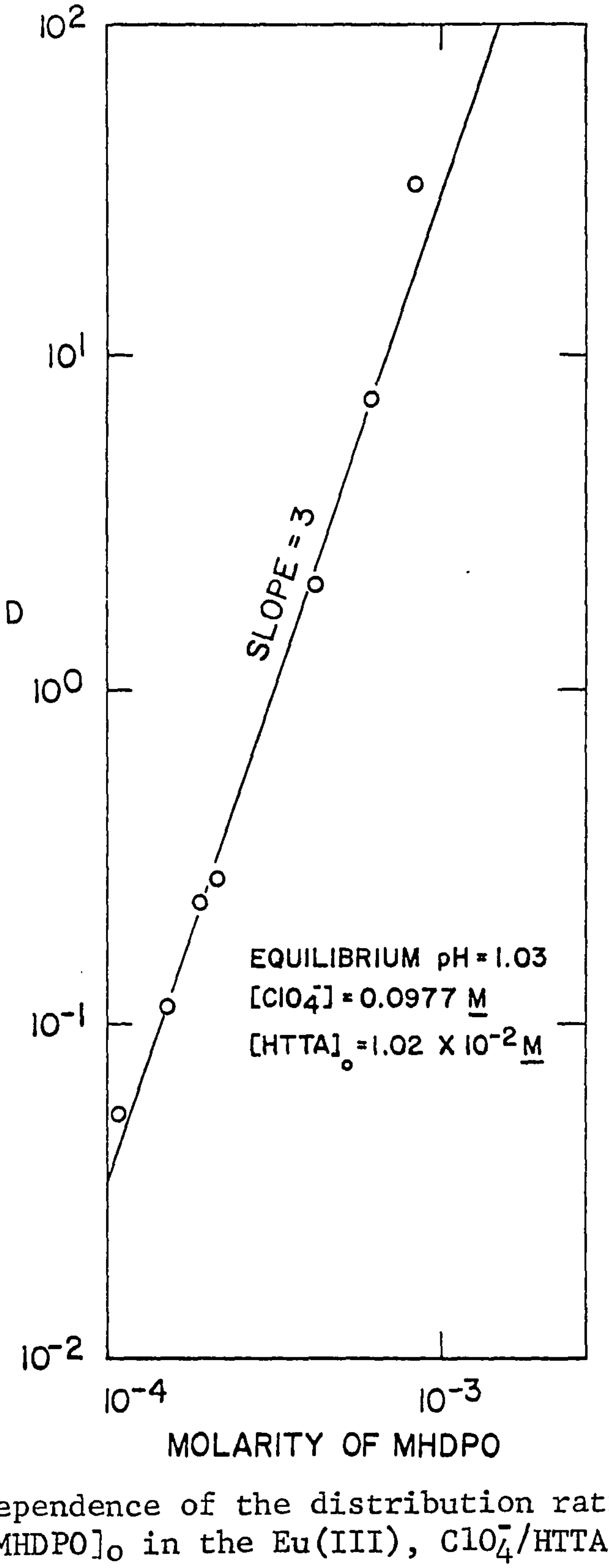


Figure 11. Dependence of the distribution ratio, D, on $[MHDPO]_o$ in the Eu(III), ClO_4^-/HTTA, MHDPO system

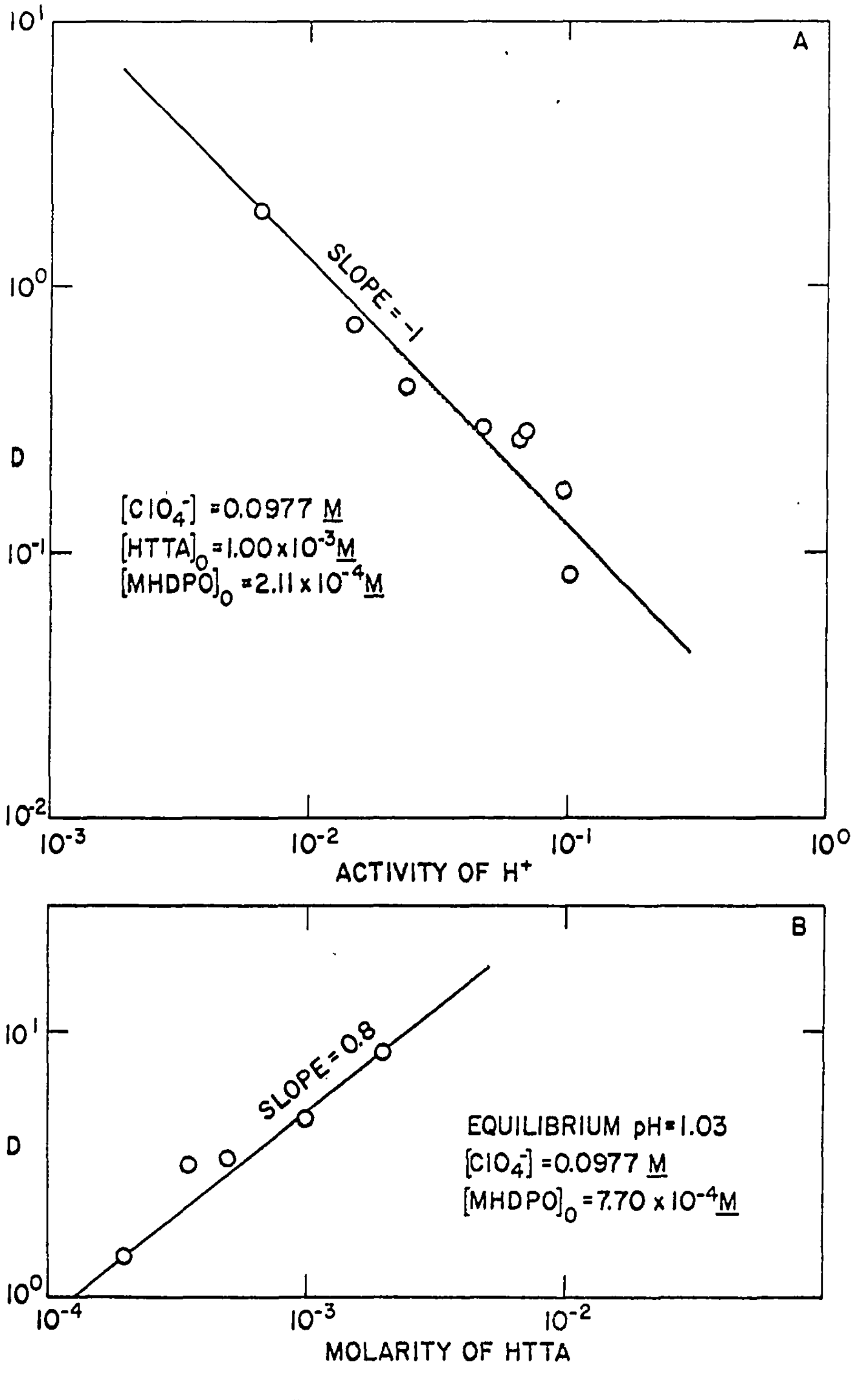


Figure 12. Dependence of the distribution ratio, D, on a_H and on $[HTTA]_o$ in the Eu(III), ClO_4^-/HTTA, MHDPO system

hydrogen ion is released upon complex formation. Correction of these data by subtracting from each distribution ratio a constant value of 0.021, the distribution given by 2.11 x 10^{-4} $\underline{M}$ MHDPO in the absence of HTTA, does not change the slope significantly but shifts the curve slightly downward. Figure 12B is a plot of log D versus log $[HTTA]_o$. The slope of this plot is only 0.8. Correction of these data by subtracting from each distribution ratio a constant value of 0.90, the distribution given by 7.70 x 10^{-4} $\underline{M}$ MHDPO in the absence of HTTA, gives a plot with a significantly different slope. A least squares treatment of the corrected data gives a slope of 1.01. This result, in conjunction with the hydrogen ion dependence, confirms that the complex in the organic phase has only one TTA in it. It is apparent that with only one TTA in the complex it is necessary for two perchlorate ions to be extracted to maintain electroneutrality. The dependence of the distribution ratio on the concentration of perchlorate ion was investigated. The concentration of perchloric acid added was constant, but the concentration of perchlorate ion was varied, each successive extraction containing a larger amount of sodium perchlorate than the previous one. Figure 13 is a plot of log (D a_H) versus log

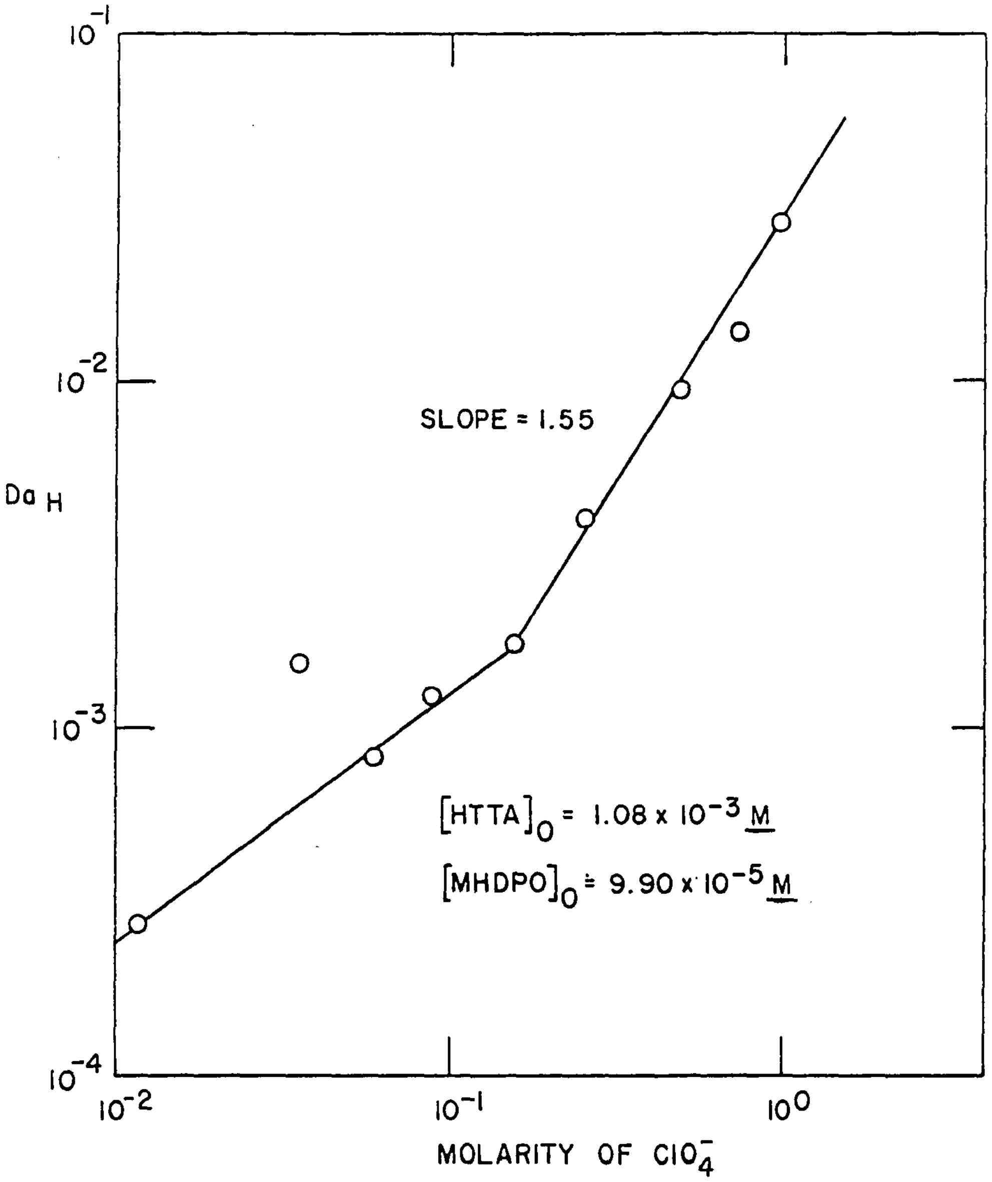


Figure 13. Dependence of the distribution ratio, D, on $[ClO_4^-]$ in the Eu(III), ClO_4^-/HTTA, MHDPO system

[ClO_4^-]. Log (D a_H) is plotted rather than log D, because it was not possible to hold the pH constant. The sodium perchlorate apparently contained some perchloric acid. The plot in Figure 13 has a maximum slope of 1.55. Because the change in the activity coefficient of the europium(III) with increasing ionic strength (0.01 to 1) is superimposed on the effect that the concentration of perchlorate ion has on the complex-forming equilibrium, one could not reasonably expect to obtain the theoretical slope of two. The slope of 1.55 does, however, seem to confirm the presence of two perchlorate ions in the europium-containing species in the organic phase. Table 11 contains the data used in constructing Figure 13.

Table 11. Dependence of D on [ClO_4^-] in the Eu^{+3}, ClO_4^-/HTTA, MHDPO system

[ClO_4^-]	a_H	D	D x a_H (x 10^3)
0.0117	0.0118	0.0234	0.275
0.0358	0.0118	0.132	1.55
0.0598	0.0118	0.0707	0.830
0.0879	0.0118	0.106	1.24
0.156	0.0118	0.150	1.76
0.252	0.0129	0.314	4.04
0.492	0.0138	0.688	9.49
0.733	0.0138	1.01	14.0
0.973	0.0158	1.81	28.7

Conditions: $[HTTA]_o = 1.08 \times 10^{-3}$ M

$[MHDPO]_o = 9.90 \times 10^{-5}$ M

The results described above show that the complex in the organic phase is $Eu(TTA)(MHDPO)_3(ClO_4)_2$. Two TTA ligands have been displaced in favor of the formation of an ion association complex. The loss of chelation energy has apparently been compensated by the formation of a much more stable complex containing three stable rings with bidentate MHDPO.

It is significant to note that europium(III) appears to be octa-coordinate in the complexes $Eu(TTA)_3(TOPO)_2$ and $Eu(TTA)_3(MHDPO)$ and probably octa-coordinate in the complexes $Eu(TTA)_3(PHDPO)$ and $Eu(TTA)_3(BHDPO)$. The europium(III) in the complex found in the organic phase in the present system also appears to be octa-coordinate, with six sites occupied by the oxygens of the three MHDPO ligands and two sites occupied by the oxygens of the TTA ligand.

The formation of the complex $Eu(TTA)(ClO_4)_2(MHDPO)_3$ is described by the equation

$$Eu^{+3} + HTTA_{(o)} + 3MHDPO_{(o)} + 2ClO_4^- \rightleftarrows Eu(TTA)(ClO_4)_2(MHDPO)_{3(o)} + H^+ \ .$$

The mixed equilibrium constant for this reaction is defined by the expression

$$K^*_{1,2,3} = \frac{[Eu(TTA)(ClO_4)_2(MHDPO)_3]_o \ a_H}{[Eu^{+3}][HTTA]_o[MHDPO]_o^3[ClO_4^-]^2}$$

which can be converted to

$$K^*_{1,2,3} = \frac{D\ a_H}{[HTTA]_o[MHDPO]_o^3[ClO_4^-]^2} \quad .$$

Table 12 contains the data used in the construction of Figures 11 and 12, as well as the values of log $K^*_{1,2,3}$ that were calculated from these data. The values of D used in calculating $K^*_{1,2,3}$ were corrected for the Eu(III) extracted by MHDPO in the absence of HTTA. The values 13.97 and 14.14 for log $K^*_{1,2,3}$ are probably the most accurate values, because the remaining value was obtained using a concentration of HTTA which is in a range where low distribution ratios are obtained. Although the low distribution gives a low value for the equilibrium constant, the slope obtained from these data remains valid.

During the investigation of this system, it was found that the material balance for the γ-activity became very poor when the concentration of MHDPO was greater than about 1 x 10^{-3} $\underline{M}$. The sum of the activity found in the two phases decreased very rapidly when the limit given above was exceeded. This seemed to indicate the formation of a third phase, and it was indeed found that when a total europium concentration of 2 x 10^{-4} $\underline{M}$ was used, a sticky, viscous third phase

Table 12. Equilibrium constant, $K^*_{1,2,3}$, for the Eu^{+3}, ClO_4^-/HTTA, MHDPO system

$[HTTA]_o$ ($\times 10^3$)	D	log $K^*_{1,2,3}$	$[MHDPO]_o$ ($\times 10^4$)	D ($\times$ 10)	log $K^*_{1,2,3}$	a_H ($\times 10^2$)	D ($\times$ 10)	log $K^*_{1,2,3}$
0.200	1.42	13.747	1.10	0.536	13.535	0.646	19.3	14.140
0.350	3.20	14.149	1.54	1.12	13.423	1.48	7.12	14.057
0.500	3.36	14.021	1.98	2.32	13.418	2.34	4.19	14.017
0.999	4.76	13.918	2.20	2.71	13.348	4.68	2.97	14.158
2.00	8.35	13.902	4.40	20.8	13.338	6.61	2.65	14.255
log $(K^*_{1,2,3})_{ave}$ =		13.97	6.60	74.4	13.364	6.92	2.86	14.312
			log $(K^*_{1,2,3})_{ave}$ =		13.41	9.55	1.71	14.204
						10.2	0.827	13.844
						log $(K^*_{1,2,3})_{ave}$ =		14.14

Conditions:

$[MHDPO]_o$ = 7.70 x 10^{-4} M

pH = 1.03

$[ClO_4^-]$ = 0.0977 M

Conditions:

$[HTTA]_o$ = 1.02 x 10^{-2} M

pH = 1.03

$[ClO_4^-]$ = 0.0977 M

Conditions:

$[HTTA]_o$ = 1.00 x 10^{-3} M

$[MHDPO]_o$ = 2.11 x 10^{-4} M

$[ClO_4^-]$ = 0.0977 M

which contained most of the europium was formed. It was also noted that as the concentration of MHDPO was raised, the distribution ratio rose very rapidly just before the third phase formation occurred (Figure 11). This observation seems to indicate the formation of a polynuclear complex at higher MHDPO concentrations. Mrochek et al. (72) have observed similar behavior when U(VI) is extracted from 1 M nitric acid with MHDPO in nonpolar solvents. Using viscosity measurements, they estimated the molecular weight of the MHDPO complex of uranium in carbon tetrachloride to be eighty times that of the TOPO complex in the same solvent. They also observed polymer formation with other metals when nonpolar solvents were used as diluents.

The method of continuous variations was applied to the study of this system in an attempt to confirm the composition of the complex and more clearly illustrate the synergic enhancement. The treatment was essentially the same as that used by Gal and Nikolić (37). The concentrations of the extractants are given by

$$[HTTA]_o + [MHDPO]_o = C \ ,$$

$$[HTTA]_o = X_{HTTA}C \ , \text{ and}$$

$$[MHDPO]_o = (1 - X_{HTTA})C \ ,$$

where X_{HTTA} is the molar fraction of HTTA present. The net distribution ratio of the tracer europium between the two phases can be expressed as

$$D = \frac{[Eu(MHDPO)_3(ClO_4)_3]_o}{[Eu^{+3}]} + \frac{[Eu(TTA)_{3-y}(ClO_4)_y(MHDPO)_n]_o}{[Eu^{+3}]} + \frac{[Eu(TTA)_3]_o}{[Eu^{+3}]} ,$$

provided there is only one mixed complex formed. If the concentrations in the expression above are replaced with their equivalents obtained from the expressions for the equilibrium constants, one obtains

$$D = D_T X_{HTTA}^3 + D_M(1 - X_{HTTA})^3 + D_{MT} X_{HTTA}^{3-y}(1 - X_{HTTA})^n ,$$

where

$$D_T = K^*_{3,0}\, a_H^{-3} C^3 ,$$

$$D_M = K^*_{0,3}[ClO_4^-]^3 C^3 , \text{ and}$$

$$D_{MT} = K^*_{3-y,y,n}[ClO_4^-]^y C^{3-y+n} a_H^{-(3-y)} .$$

It is easily seen that if $X_{HTTA} = 0$ or $X_{HTTA} = 1$, one obtains $D = D_M$ or $D = D_T$, respectively. A corrected distribution ratio can now be written:

$$Q_x = D - D_T X_{HTTA}^3 - D_M(1 - X_{HTTA})^3 = D_{MT} X_{HTTA}^{3-y}(1 - X_{HTTA})^n .$$

Q_x is a simple function of X_{HTTA}. Differentiation of this equation and insertion of $X_{HTTA} = X_{max}$ when $dQ_x/dX_{HTTA} = 0$ gives

$$\frac{3 - y}{n} = \frac{X_{max}}{1 - X_{max}} \; .$$

A plot of Q_x versus X_{HTTA} will provide a value for X_{max}, and the ratio (3 - y)/n can be calculated from this quantity. Table 13 gives data obtained from a continuous variations treatment of the Eu(III), ClO_4^-/HTTA, MHDPO system. Figure 14B is a plot of Q_x versus X_{HTTA}. The maximum occurs near $X_{HTTA} = 0.25$, supporting the previous conclusions that (3 - y)/n = 1/3 and that the complex in the organic phase is

Table 13. Continuous variations treatment of the Eu^{+3}, ClO_4^-/HTTA, MHDPO system

X_{HTTA}	D	D_M[a]	Q_x	D_{MT}
0.901	3.84×10^{-3}	0.0010	0.00284	3.15
0.504	8.63×10^{-2}	0.0321	0.0541	0.88
0.101	2.53×10^{-1}	0.191	0.0620	0.85
0.040	2.84×10^{-1}	0.233	0.0510	1.44
0.020	2.80×10^{-1}	0.248	0.0320	1.70
0.000	2.63×10^{-1}			

Conditions: $C = 5.00 \times 10^{-4}$ M

pH = 1.17

$[ClO_4^-] = 0.0872$ M

[a] Calculated as $(1 - X)^3$ times the value of D at $X_{HTTA} = 0$.

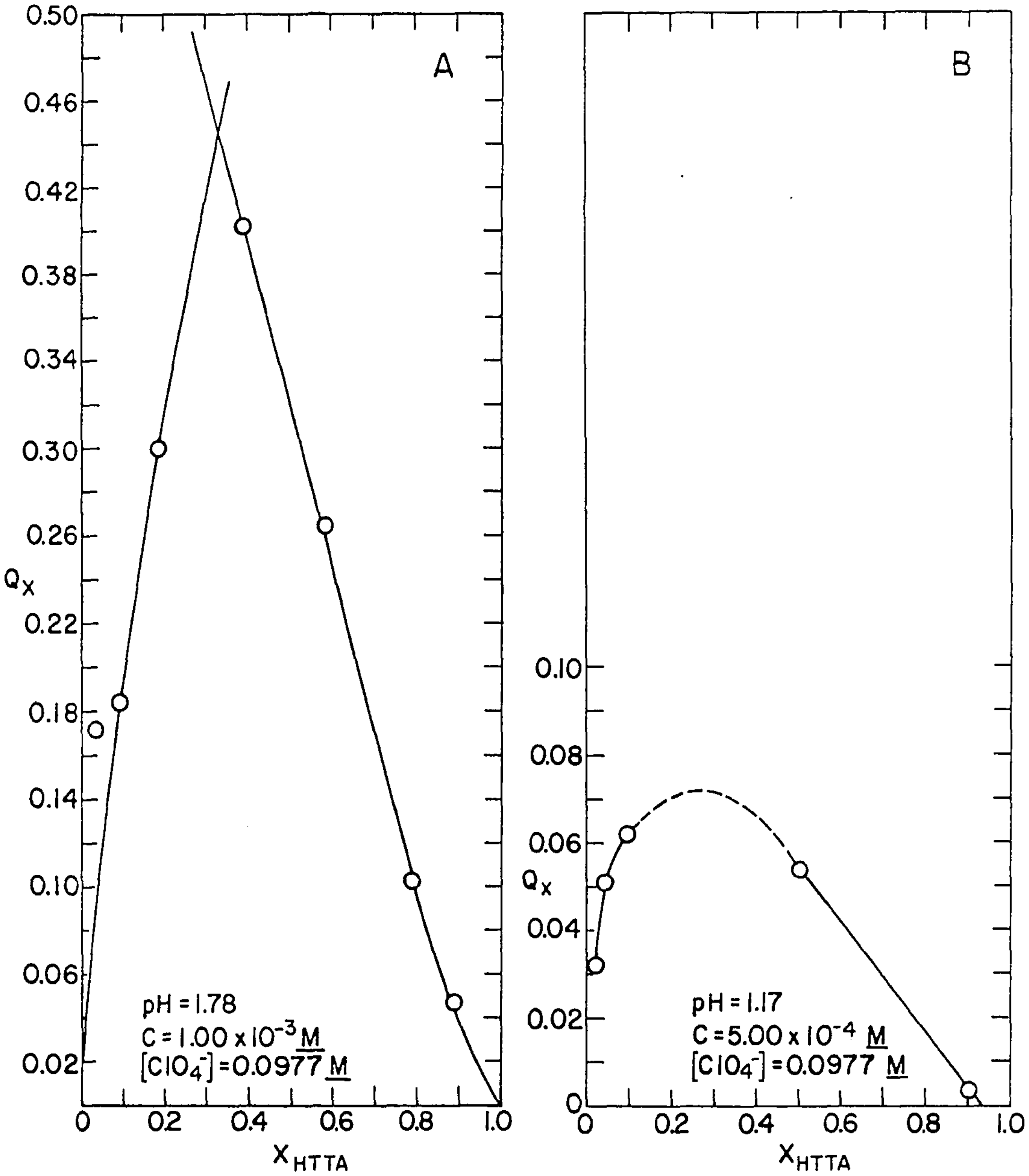


Figure 14. Application of the method of continuous variations to the Eu(III), ClO_4^-/HTTA, MHDPO, 1,2-dichlorobenzene system (A) and the Eu(III), ClO_4^-/HTTA, MHDPO system (B)

$Eu(TTA)(MHDPO)_3(ClO_4)_2$. Table 13 includes values of D_{MT}. D_{MT} is nearly independent of X_{HTTA} except at low or high X_{HTTA}; therefore, only one mixed complex appears to be formed.

The rate of reaction was studied briefly to determine the shaking time required to establish equilibrium. The data are given in Table 14. Analysis of these data leads to the conclusion that the behavior is no different than that observed for the Eu(III), Cl^- or ClO_4^-/HTTA, TOPO systems, even though the complex in the organic phase is quite different in the present system. These results seem to support the conclusions reached in the rate of reaction studies

Table 14. Dependence of D on time in the Eu^{+3}, ClO_4^-/HTTA, MHDPO system

Time (hours)	D
0.25	0.474
0.50	0.542
1.00	0.306
1.50	0.337
2.00	0.294
9.00	0.314

Conditions: $[HTTA]_o = 1.02 \times 10^{-2}$ $\underline{M}$

$[MHDPO]_o = 2.20 \times 10^{-4}$ $\underline{M}$

$[ClO_4^-] = 0.0977$ $\underline{M}$

pH = 1.04

described earlier.

The Eu(III), ClO_4^-/HTTA, MHDPO, 1,2-dichlorobenzene system

The foregoing solvent extraction system, under certain conditions, apparently gives polynuclear complex formation followed by the formation of a third phase. It was decided that a more polar diluent would eliminate these difficulties; therefore, 1,2-dichlorobenzene was substituted for cyclohexane and the system was restudied.

The method of continuous variations was applied to this system in the same manner as it was applied to the foregoing system. Figure 14A is a plot of Q_X versus X_{HTTA}. The maximum occurs at $X_{HTTA} = 0.33$, apparently indicating that there may be twice as many MHDPO ligands as TTA ligands in the europium-containing species in the organic phase. Table 15 contains the data used in the construction of Figure 14A as well as the values for D_{MT} that were calculated from these data. The values of D_{MT} are fairly constant near the maximum value of Q_X, but they become much larger at low or high X_{HTTA}. These deviations may be the result of the formation of more than one mixed complex in the organic phase.

In order to establish the number of TTA and MHDPO ligands in the europium-containing species in the organic phase, it

Table 15. Continuous variations treatment of the Eu^{+3}, ClO_4^-/HTTA, MHDPO, 1,2-dichlorobenzene system

X_{HTTA}	D	D_M[a]	Q_x	D_{MT}
1.00	8.61×10^{-5}			
0.958	1.83×10^{-2}	0.02		
0.894	6.69×10^{-2}	0.02	0.0469	46.6
0.790	1.31×10^{-1}	0.02	0.111	17.1
0.585	2.82×10^{-1}	0.02	0.262	8.2
0.389	4.26×10^{-1}	0.02	0.406	7.3
0.190	3.43×10^{-1}	0.043	0.300	6.8
0.0944	2.46×10^{-1}	0.062	0.184	8.5
0.0376	2.45×10^{-1}	0.074	0.171	26.3
0.000	1.29×10^{-1}			

Conditions: $C = 1.00 \times 10^{-3}$ M

$pH = 1.78$

$[ClO_4^-] = 0.0977$ M

[a] Values estimated from Figure 17.

was necessary to supplement the method of continuous variations with other data. The law of mass action was applied to this system in the same manner as it was applied to the previous systems. Figure 15 is a plot of log D versus log $[HTTA]_o$. The slope of the line is 1.5. Figure 16 is a plot of log D versus log a_H. The line has a slope of -1.5 when a_H is greater than 0.01 and a slope that is more negative than -1.5 at lower values of a_H. Figure 17 contains two plots of log D versus log $[MHDPO]_o$. The data for the top curve were

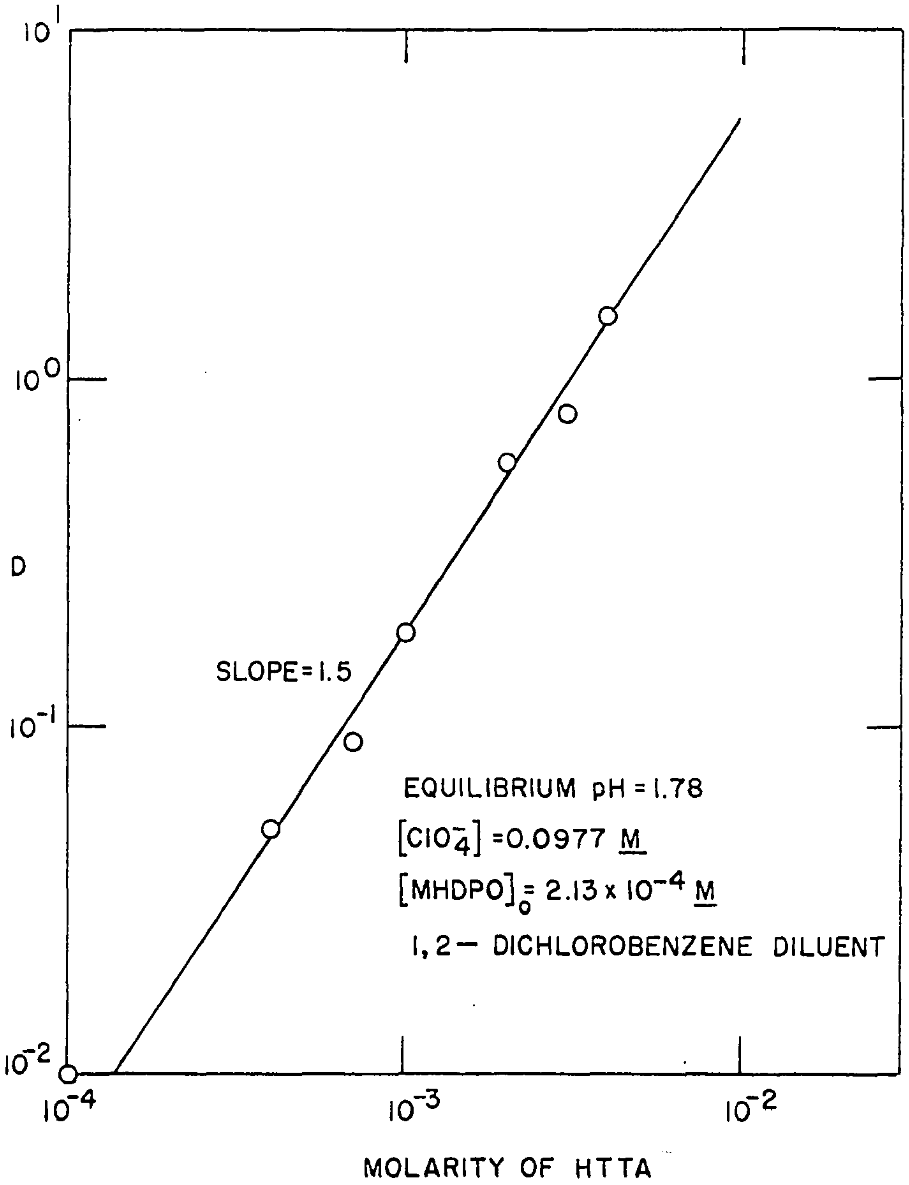


Figure 15. Dependence of the distribution ratio, D, on $[HTTA]_o$ in the Eu(III), ClO_4^-/HTTA, MHDPO, 1,2-dichlorobenzene system

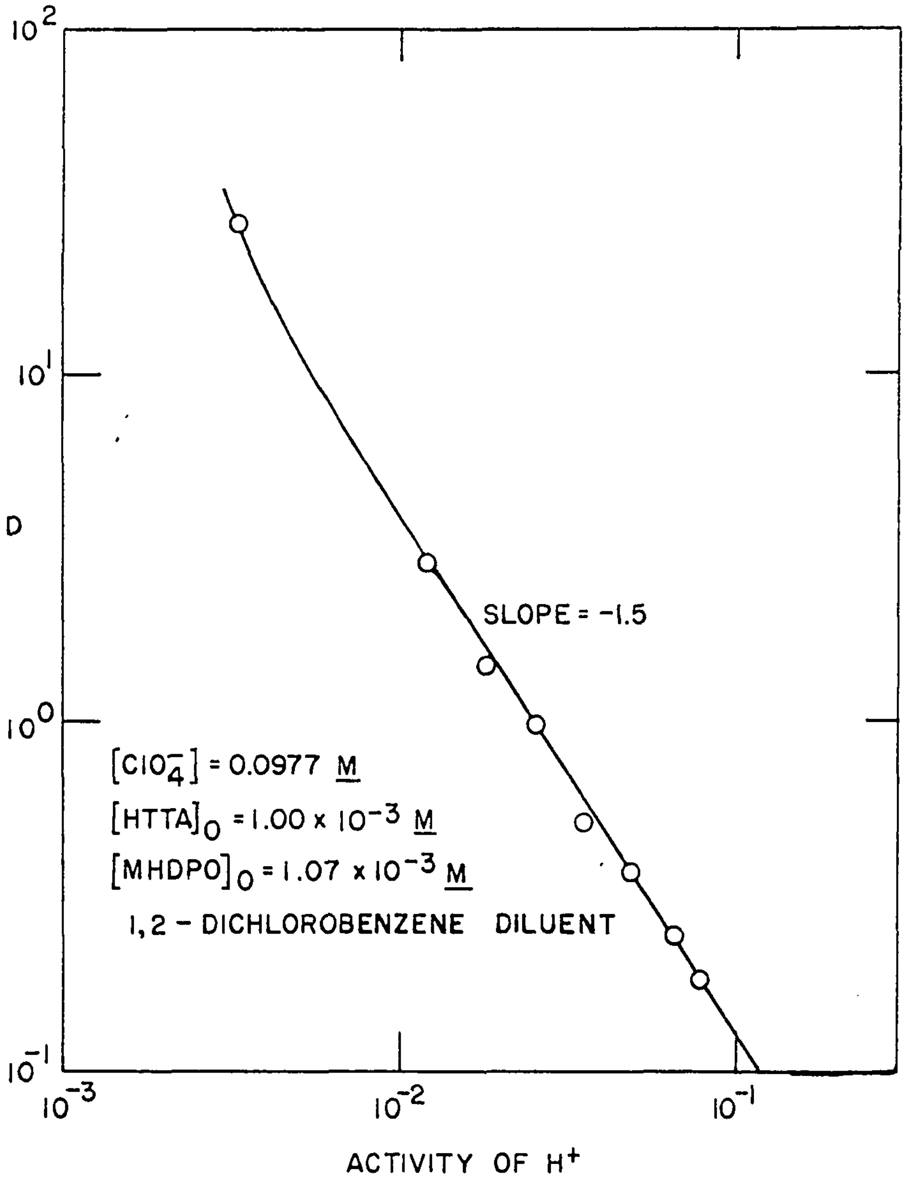
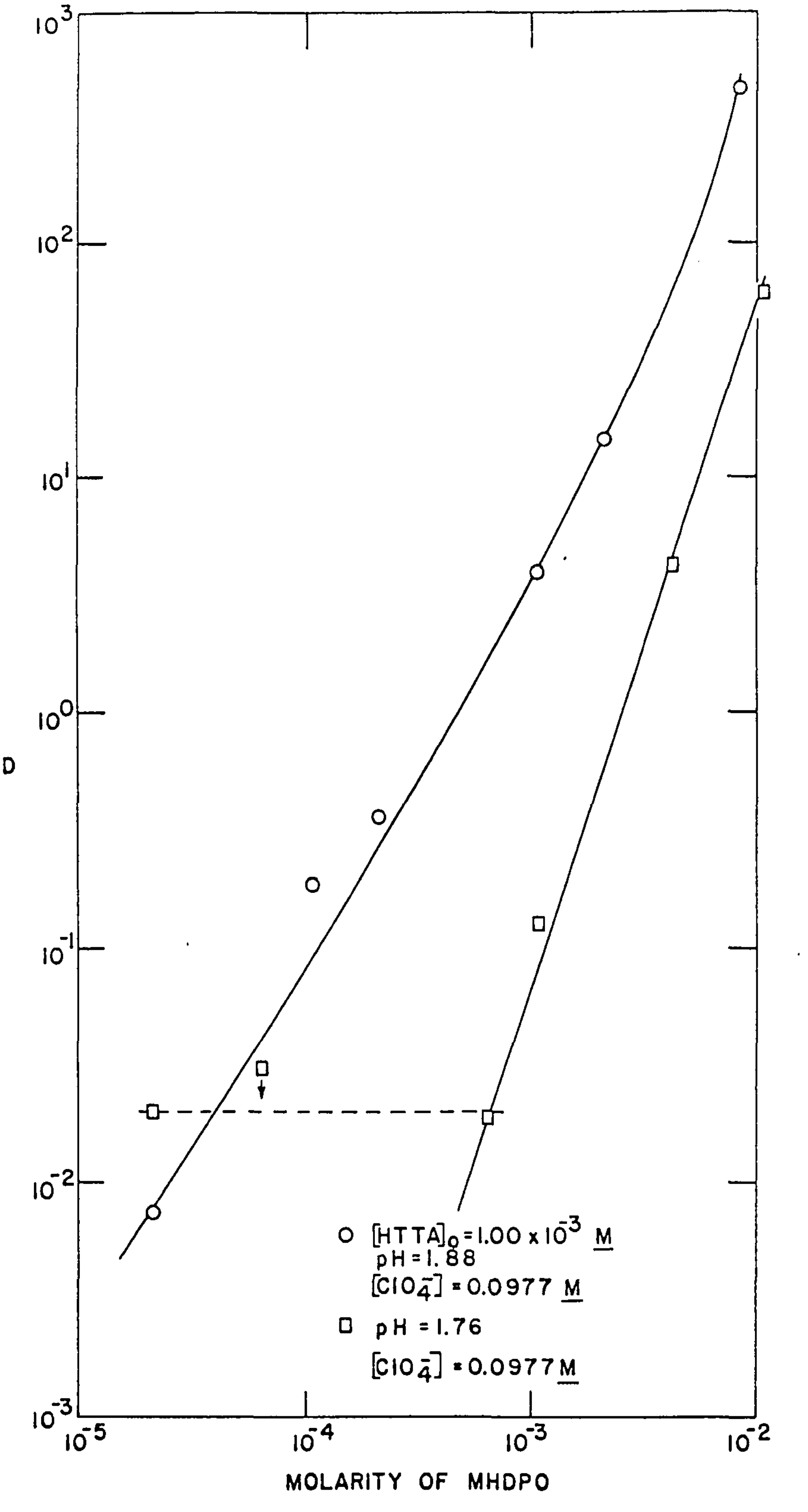


Figure 16. Dependence of the distribution ratio, D, on a_H in the Eu(III), ClO_4^-/HTTA, MHDPO, 1,2-dichlorobenzene system

Figure 17. Dependence of the distribution ratio, D, on $[MHDPO]_o$ in the Eu(III), ClO_4^-/HTTA, MHDPO, 1,2-dichlorobenzene system and in the Eu(III), ClO_4^-/MHDPO, 1,2-dichlorobenzene system


10^3
10^2
10^1
10^0
10^{-1}
10^{-2}
10^{-3}
D
10^{-5}
10^{-4}
10^{-3}
10^{-2}
MOLARITY OF MHDPO
○ $[HTTA]_0 = 1.00 \times 10^{-3}$ M
pH = 1.88
$[ClO_4^-] = 0.0977$ M
□ pH = 1.76
$[ClO_4^-] = 0.0977$ M

obtained with 1.00×10^{-3} $\underline{M}$ HTTA in the organic phase, and the data for the other curve were obtained in the absence of HTTA. In the absence of HTTA the data obtained at MHDPO concentrations above 5×10^{-4} $\underline{M}$ indicate that $Eu(MHDPO)_3(ClO_4)_3$ is the europium-containing species in the organic phase, but the data for concentrations of MHDPO that are less than 5×10^{-4} $\underline{M}$ indicate that the distribution ratio is independent of the concentration of MHDPO. The slope of the curve in Figure 17 obtained for the mixed ligand system varies from 1.5 to 2 when $[MHDPO]_o$ is less than 2×10^{-3} $\underline{M}$ and increases very rapidly above 2×10^{-3} $\underline{M}$ MHDPO. Correction of this curve for the europium extracted by MHDPO in the absence of HTTA does not alter the slope significantly; however, when this correction is applied to the data for Figures 15 and 16, the slopes become 1.7 and -1.7, respectively. Figure 18 shows that the perchlorate ion is involved in the extraction equilibrium; however, the value of the slope (1.1) only indicates that at least one perchlorate ion is involved in the equilibrium. The data used in the construction of Figures 15-18 are contained in Tables 16 and 17.

The data from the application of the law of mass action showed that the dependence of D on $[MHDPO]_o$ and $[HTTA]_o$ is

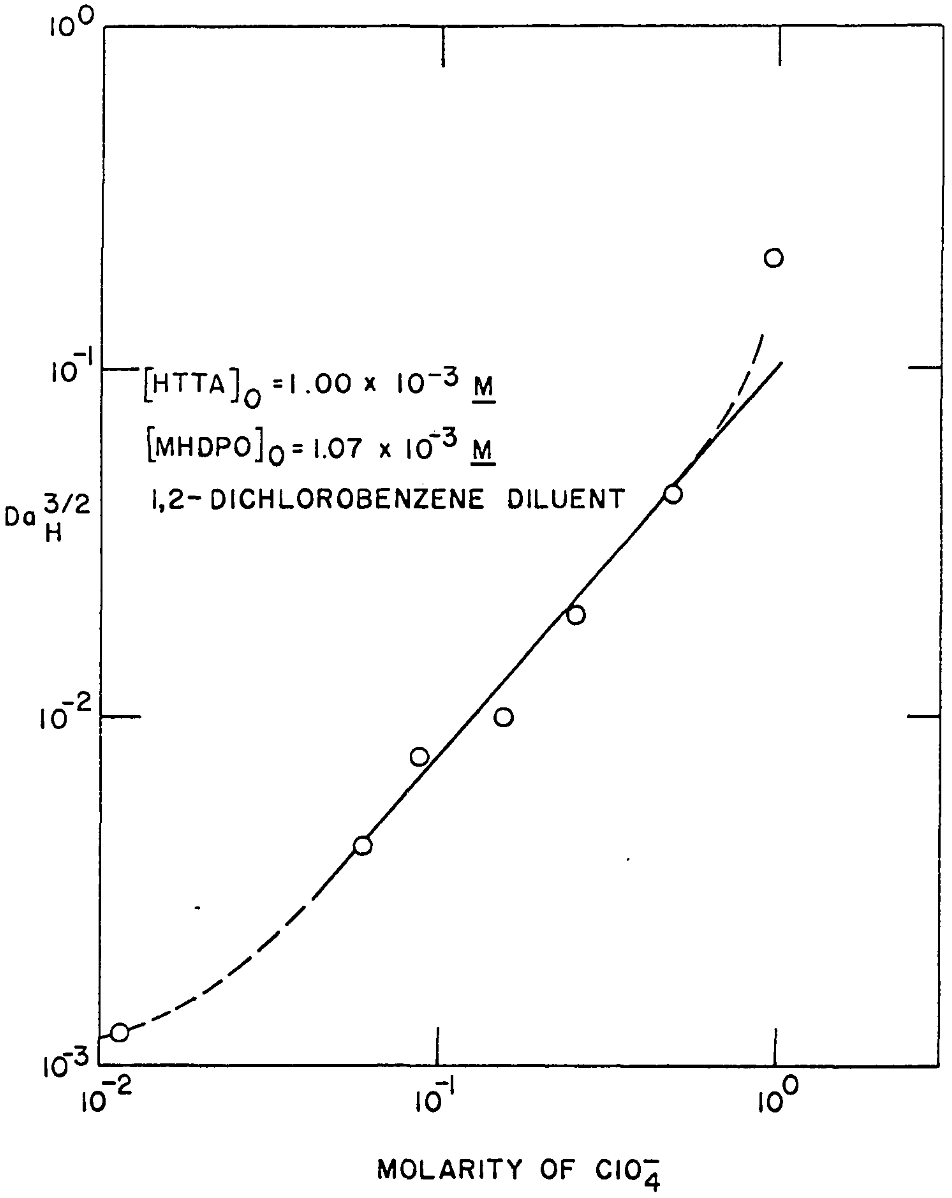


Figure 18. Dependence of the distribution ratio, D, on $[ClO_4^-]$ in the Eu(III), ClO_4^-/HTTA, MHDPO, 1,2-dichlorobenzene system

Table 16. Data for the Eu^{+3}, ClO_4^-/HTTA, MHDPO, 1,2-dichlorobenzene system

$[HTTA]_o$ (x 10^3)	D (x 10)	a_H (x 10^2)	D	$[MHDPO]_o$ (x 10^4)	D
0.100	0.101	0.339	27.5	0.213	0.00748
0.400	0.515	1.20	2.86	1.07	0.186
0.700	0.912	1.78	1.44	2.13	0.359
1.00	1.89	2.51	0.987	10.7	3.96
2.00	5.86	3.47	0.524	21.3	14.2
3.00	7.97	4.79	0.376	85.3	469
4.00	15.2	6.46	0.244		
		7.76	0.185		
Conditions: $[MHDPO]_o$ = 2.13×10^{-4} M pH = 1.78 $[ClO_4^-]$ = 0.0977 M		Conditions: $[HTTA]_o$ = 1.00×10^{-3} M $[MHDPO]_o$ = 1.07×10^{-3} M $[ClO_4^-]$ = 0.0977 M		Conditions: $[HTTA]_o$ = 1.00×10^{-3} M $[ClO_4^-]$ = 0.0977 M pH = 1.88	

$[ClO_4^-]$ (x 10)	D	a_H (x 10^2)	D x $a_H^{3/2}$ (x 10^2)
0.115	1.02	1.15	0.125
0.596	2.74	1.35	0.430
0.877	4.50	1.44	0.778
1.56	5.63	1.48	1.01
2.52	9.54	1.62	1.97
4.92	17.4	1.86	4.42
9.72	56.9	2.40	21.2

Conditions:

$[HTTA]_o$ = 1.00×10^{-3} M

$[MHDPO]_o$ = 1.07×10^{-3} M

Table 17. Extraction of Eu^{+3} from perchlorate medium with MHDPO in 1,2-dichlorobenzene

$[MHDPO]_o$ ($\times 10^4$)	D
0.213	0.0202
0.640	0.0301
6.40	0.0190
10.7	0.129
42.6	4.23
107	61.2

Conditions: pH = 1.76

$[ClO_4^-]$ = 0.0977 M

nearly second power, that the dependence of D on a_H is nearly negative second power, and that the dependence of D on $[ClO_4^-]$ is approximately first power; therefore, these data seem to indicate that the most likely mixed ligand complex in the organic phase in most of the concentration range considered is $Eu(TTA)_2(MHDPO)_2ClO_4$. On the other hand, the results of the application of the method of continuous variations indicated a complex having twice as many MHDPO ligands as TTA ligands. Therefore, the results of the method of investigation used in this study are rather inconclusive for this system in that they do not allow one to assign a stoichiometry to a mixed ligand complex with certainty. The data do, however, show that there is a large synergic enhancement of extraction, that there is mixed complex formation, and that the mixed complex probably contains at least one perchlorate ion. The fact that the slopes generally increased with increasing ligand concentration, increasing perchlorate concentration, or decreasing a_H seems to indicate that the composition of the predominant mixed ligand complex is dependent on the conditions and that there are probably mixtures of complexes present under most conditions.

Solvent Extraction-Molar Ratio Study

In the previous work the stoichiometries of the synergic complexes of europium were established using a trace concentration (10^{-8} $\underline{M}$) of europium. In the work described in this section, the stoichiometries were determined at a higher concentration (2×10^{-4} $\underline{M}$) of europium to show that the same complexes are formed at macro levels of europium(III) and to confirm the formulae by a different method. The experimental details are given in EXPERIMENTAL.

This study is based on the fact that europium(III) is extracted very poorly by HTTA in the absence of a synergist. The concentration of $Eu(TTA)_3$ will be very small in comparison to that of the mixed complex, and it will contribute very little to the per cent extraction of europium or the fluorescence of the organic phase.

The formation of the synergic complex is represented by the following reaction:

$$Eu^{+3} + 3HTTA_{(o)x's} + nL \rightleftarrows Eu(TTA)_3L_n + 3H^+ ,$$

where the subscript "x's" indicates that HTTA is always in excess and at a constant total concentration. If the concentration of H^+ is placed at a low level ($a_H = 3.2 \times 10^{-6}$), the equilibrium is shifted far to the right and the limiting quantity in the extraction becomes the amount of phosphine oxide available. The percentage of the europium extracted will, therefore, reach 100 when the stoichiometric amount of organophosphorus compound is added. The extraction of europium was followed using two methods: 1) spectrophotometric analysis of the aqueous phase and 2) measurement of the fluorescence of the organic phase (a relative analysis for europium). The spectrophotometric and the fluorometric methods were described in EXPERIMENTAL. Figure 19 shows the apparent fluorescent spectrum of the synergic complex formed when europium is extracted into a mixture of excess HTTA plus excess TOPO. The large band at 617 mμ was the one used in the fluorometric measurements.

Figure 20A shows the relative fluorescence of the organic

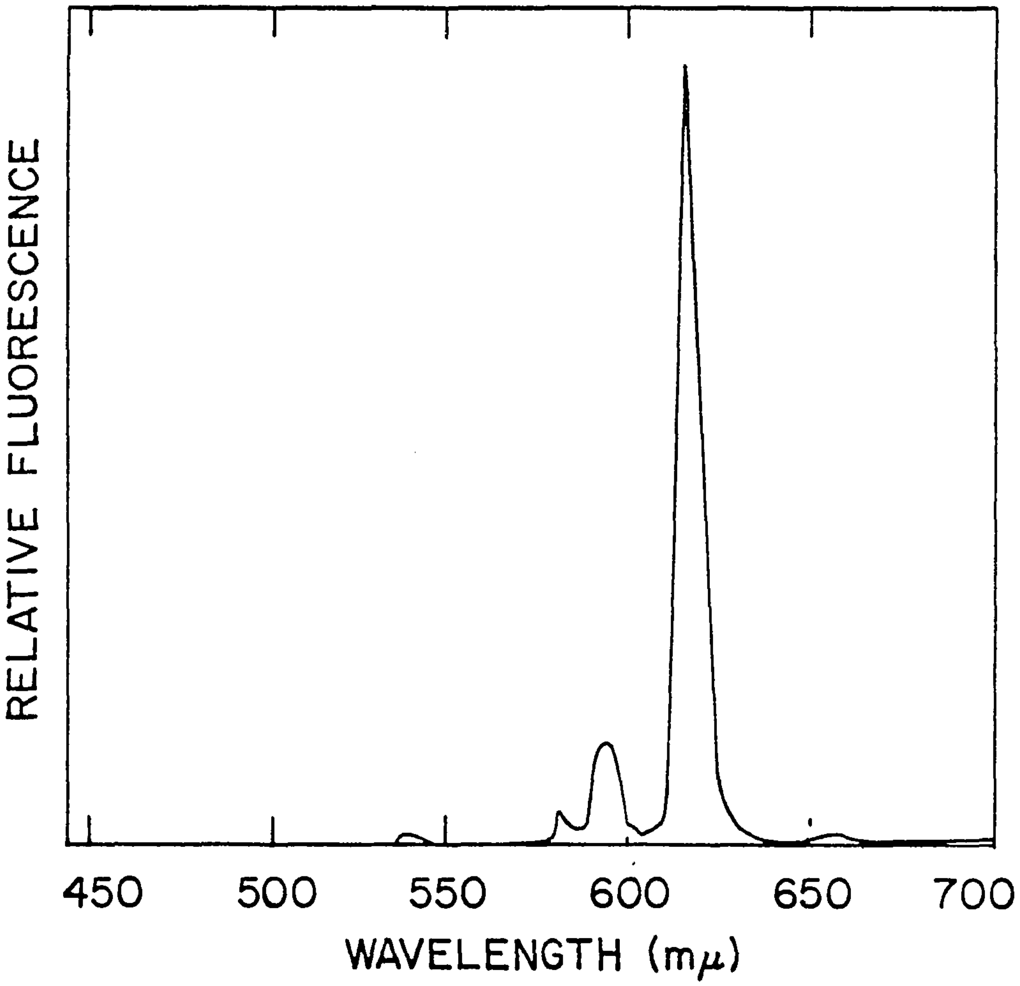
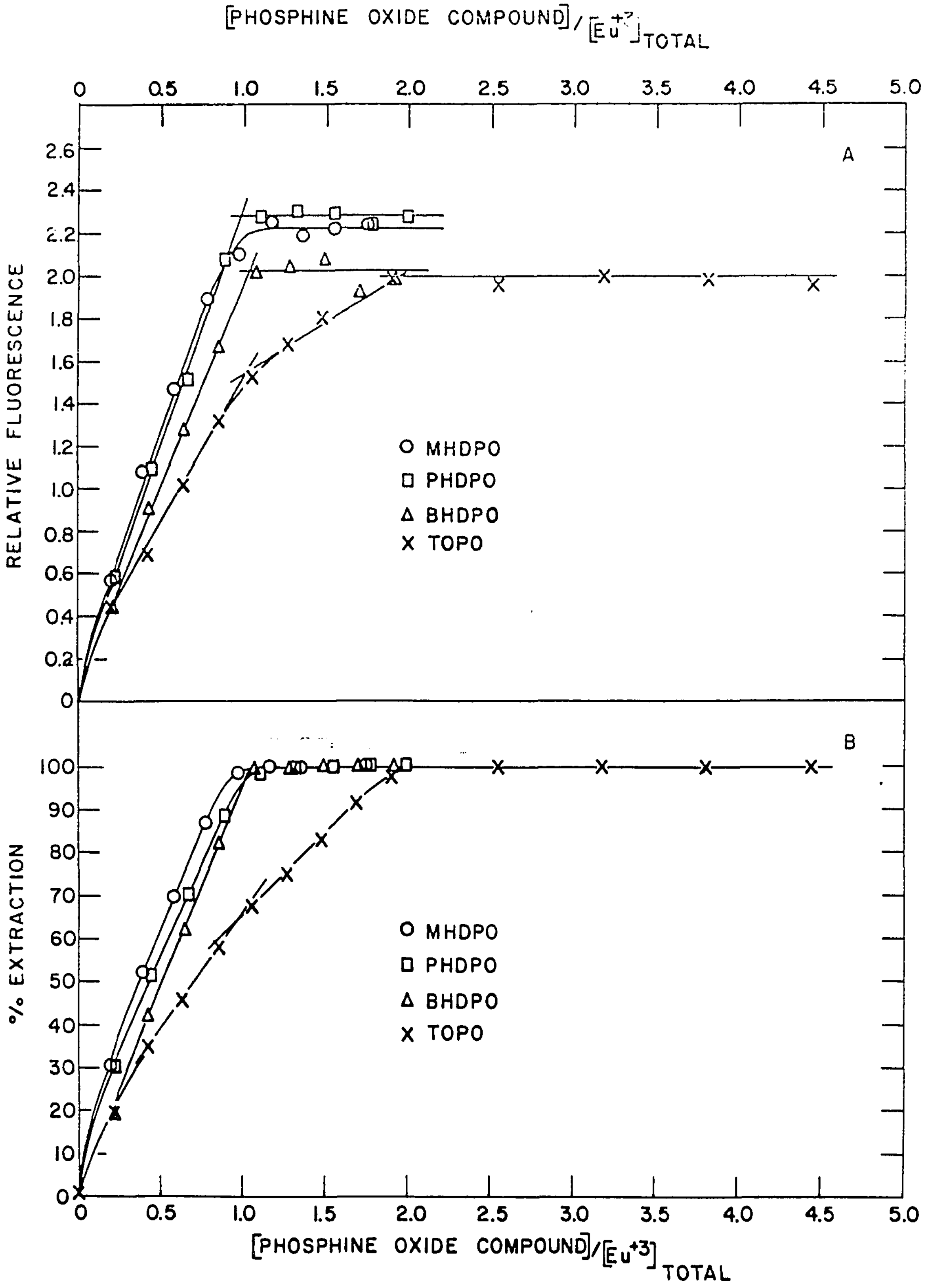


Figure 19. The apparent fluorescent spectrum of $Eu(TTA)_3$ $(TOPO)_2$

Figure 20. Dependence of the amount of Eu(III) extracted (relative fluorescence also) on the ratio of the concentration of organophosphorus compound to the original concentration of europium in the aqueous phase in the Eu(III), OAc^-/HTTA, organophosphorus compound systems


[PHOSPHINE OXIDE COMPOUND]/[Eu+3]TOTAL
0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
A
RELATIVE FLUORESCENCE
2.6
2.4
2.2
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0
○ MHDPO
□ PHDPO
△ BHDPO
X TOPO
B
% EXTRACTION
100
90
80
70
60
50
40
30
20
10
0
○ MHDPO
□ PHDPO
△ BHDPO
X TOPO
[PHOSPHINE OXIDE COMPOUND]/[Eu+3]TOTAL

phase as a function of the molar ratio of the concentration of the organophosphorus compound to the original concentration of europium in the aqueous phase, and Figure 20B shows the percentage of the europium extracted as a function of the same molar ratio. The systems involving the bifunctional phosphine oxides all reach 100% extraction (constant fluorescence) at a molar ratio of 1:1, indicating that the europium-containing species in the organic phase is a 1:1 adduct in each case. The system involving TOPO, however, shows a different behavior. The plot of the percentage extraction (fluorescence also) as a function of the molar ratio increases at one slope until a molar ratio of 1:1 is reached and then continues to increase at another slope until 100% extraction (constant fluorescence) is achieved at a molar ratio of 2:1, indicating that 1:1 and 2:1 adducts are formed successively. The ratios given above indicate that the predominant europium-containing species in the organic phase are $Eu(TTA)_3(MHDPO)$, $Eu(TTA)_3(PHDPO)$, $Eu(TTA)_3(BHDPO)$, and $Eu(TTA)_3(TOPO)_2$. It appears that $Eu(TTA)_3(TOPO)$ also forms at low concentrations of TOPO. These stoichiometries agree well with those found earlier in the extraction of europium(III) from chloride medium.

The fact that the Eu(III), OAc^-/HTTA, bifunctional phosphine oxide systems all achieve 100% extraction (constant fluorescence) at a molar ratio of 1:1 but the Eu(III), OAc^-/HTTA, TOPO system does not achieve this level until a molar ratio of 2:1 is reached, seems to indicate that the 1:1 complexes with the bifunctional phosphine oxides are either more soluble in the organic phase or more stable than the 1:1 complex with TOPO. If the diphosphine oxides are bidentate ligands and displace both waters upon reacting with $Eu(TTA)_3(H_2O)_2$ and if TOPO displaces only one water in the same reaction, this would give the 1:1 adducts with the diphosphine oxides a higher solubility in the organic phase. In the foregoing statement it was, of course, assumed that the complex of europium with TTA as the only ligand has the same composition in solution as it does in the solid state. Because the diphosphine oxides are less basic than TOPO, any additional stability of the 1:1 diphosphine oxide adduct may be due to the formation of a ring with the metal. In either of the explanations given above, the formation of an adduct in which the diphosphine oxides are bidentate seems to be indicated.

Taketatsu and Banks (105) made a study similar to the one described above on the Ln(III), OAc^-/HTTA, TOPO, toluene systems, where Ln(III) is Ho(III), Er(III), or Nd(III). They used the absorbance at certain characteristic wavelengths to follow the extraction. Figure 21 shows their data for absorbance as a function of the molar ratio of TOPO to rare earth at a constant concentration of HTTA. It is easily seen that they found breaks at molar ratios of 1:1 and 2:1, in agreement with what was found in the present work. Figure 22 shows their data for absorbance or percentage extraction as a function of the molar ratio of HTTA to the rare earth at a constant concentration of TOPO. These data confirm that there are three TTA ligands in the complex in the organic phase.

Loading Capacity Experiment

Evidence was presented in the preceding section for the formation of a 1:1 adduct of $Eu(TTA)_3$ with TOPO. Additional evidence for the formation of this complex is shown in this section.

The loading capacity of a 5.14×10^{-3} $\underline{M}$ solution of TOPO in cyclohexane was determined as described in EXPERIMENTAL. It was found that the ratio of TOPO to "tagged" $Eu(TTA)_3(H_2O)_2$ in the saturated solution was 1.07, indicating that a 1:1 adduct was formed.

The evidence presented in this thesis, along with the

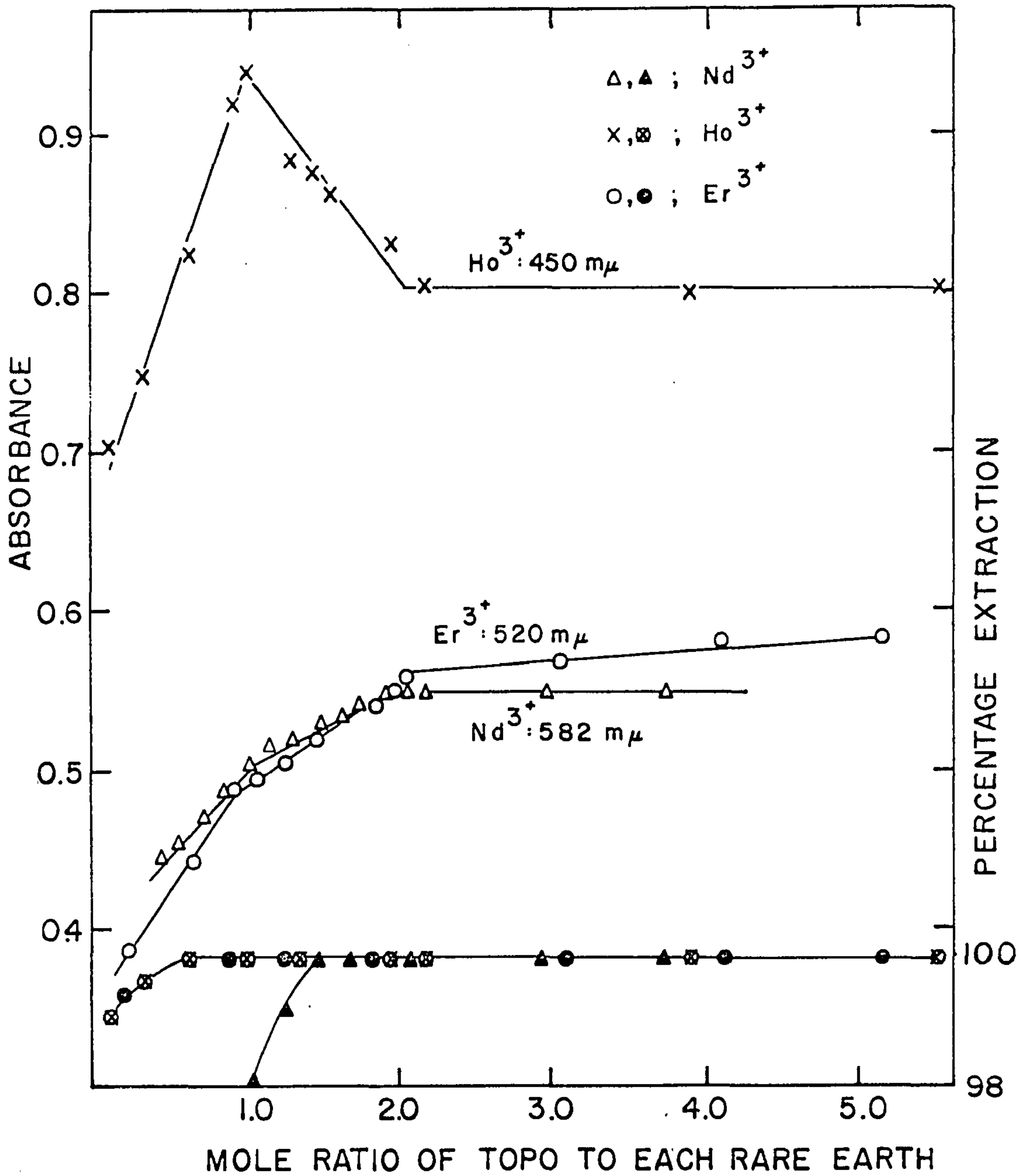


Figure 21. Dependence of the absorbance on the ratio of $[TOPO]_o$ to the original concentration of each lanthanide in the aqueous phase in the Ln(III), OAc^-/HTTA, TOPO, toluene systems

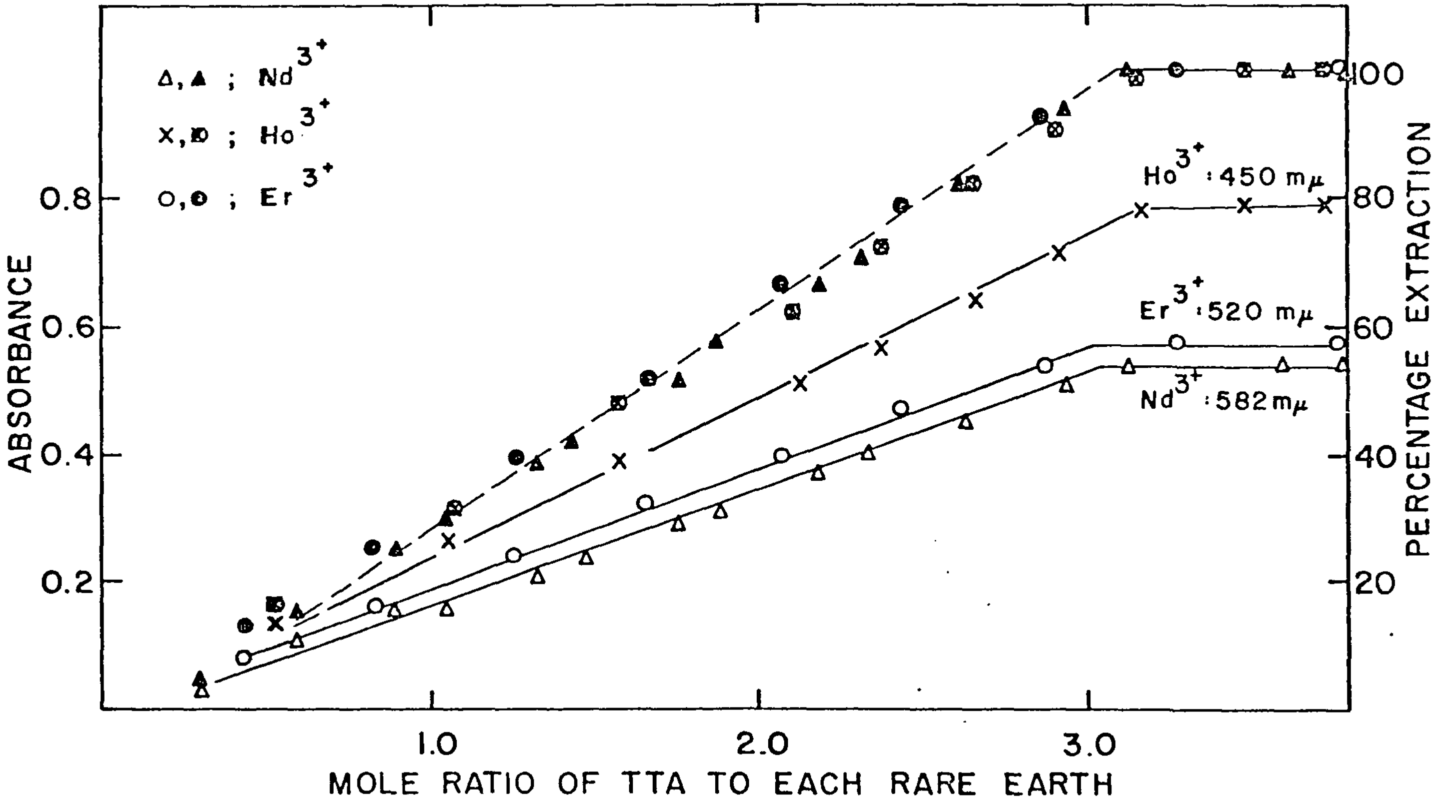


Figure 22. Dependence of the absorbance on the ratio of $[HTTA]_o$ to the original concentration of each lanthanide in the aqueous phase in the Ln(III), OAc^-/HTTA, TOPO, toluene systems

absorption data of Taketatsu and Banks (105), appears to be the only direct evidence for the formation of a 1:1 adduct of a tris-TTA chelate of a lanthanide, which also forms a 2:1 adduct. Sekine and Dyrssen (95,96,97) have inferred the existence of such adducts by applying a curve-fitting technique to data from solvent extraction measurements, but they gave no direct evidence.

Fluorometric Molar Ratio Study

The mechanical details of this study are given in EXPERIMENTAL. Figure 23 presents plots of the relative fluorescence of europium at 617 mμ as a function of the molar ratio of the individual phosphine oxides to the total europium concentration. The plot for TOPO has one break at a molar ratio of 1:1 and another break at a molar ratio of 2:1, indicating that 1:1 and 2:1 adducts are formed successively. The plots for the diphosphine oxides all reach a constant fluorescent intensity at a molar ratio of 1:1, possibly indicating the formation of 1:1 adducts. The very steep rise in fluorescence until a molar ratio of 0.5:1 is reached may indicate the formation of the hemisolvate that was discussed in connection with the Eu(III), Cl^-/HTTA, MHDPO solvent extraction system, followed by conversion to the monosolvate. Another

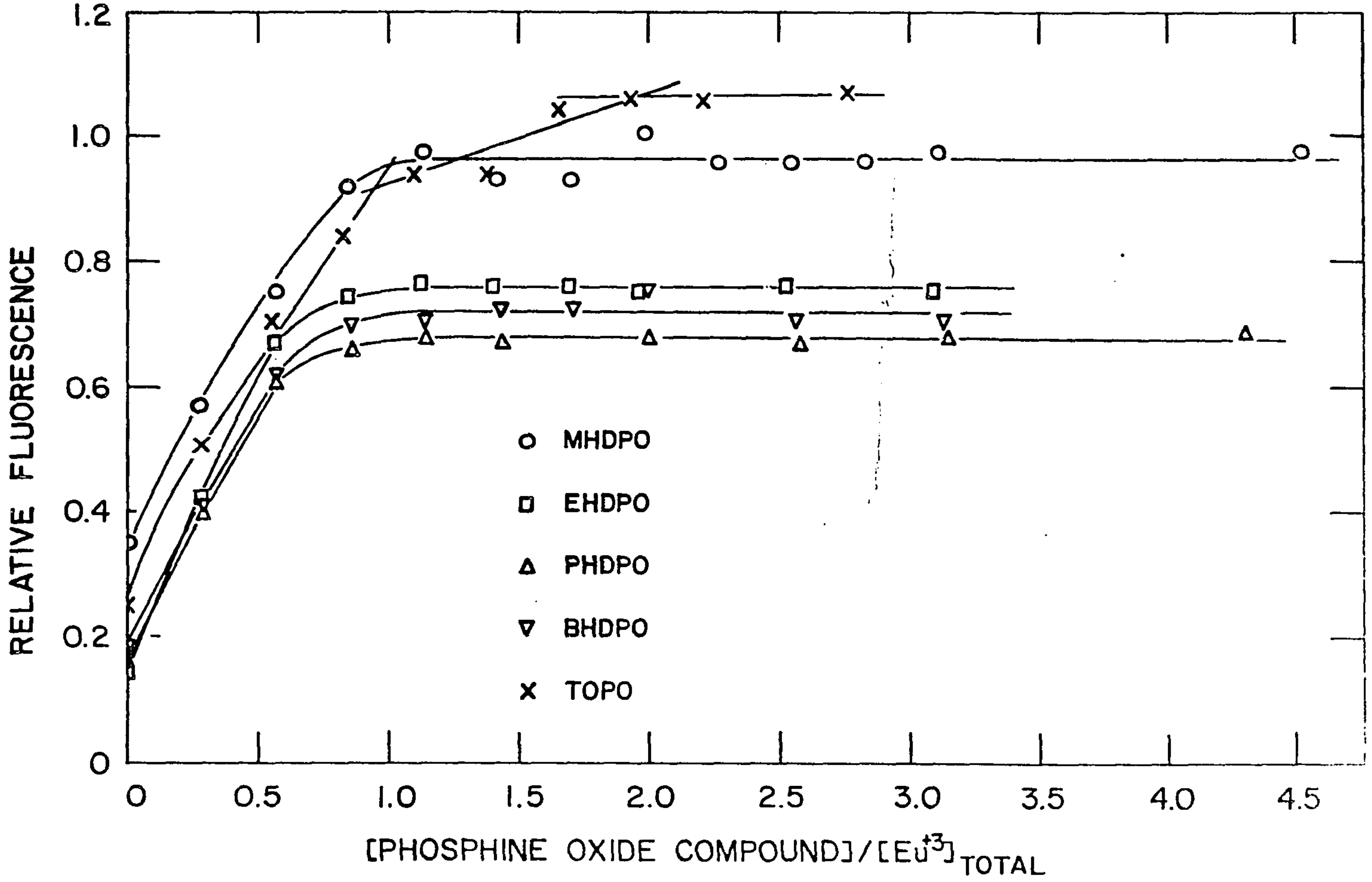


Figure 23. Dependence of the relative fluorescence on the ratio of the concentration of organophosphorus compound to the total concentration of europium

possibility, of course, is the formation of the hemisolvate as the only complex in this range of concentrations. The very gentle rise in the intensity of the fluorescence between 0.5:1 and 1:1 could be due to driving the formation of the hemisolvate to completion. On the basis of these data, it is not possible to distinguish between the two possibilities given above. In either case the formation of a hemisolvate seems to be consistent with the data. Although the data seem to indicate that a hemisolvate is formed with the diphosphine oxides, it should be remembered that the solution here differs from the organic phase in a solvent extraction system in that it was not saturated with water and the aqueous acid.

Irving and Edgington (51) proposed that the formation of synergic complexes occurs by replacing water in the TTA complex of the metal with the synergist. It was shown above that TOPO forms 1:1 and 2:1 adducts of $Eu(TTA)_3$, when it is reacted with $Eu(TTA)_3(H_2O)_2$. The formation of these adducts is probably best described by the reaction

$$Eu(TTA)_3(H_2O)_2 + nTOPO \rightleftharpoons Eu(TTA)_3(H_2O)_{2-n}(TOPO)_n + nH_2O \ .$$

Therefore, in the case of TOPO, it has been shown that the same complexes as are formed in the solvent extraction process can be formed by replacing water from $Eu(TTA)_3(H_2O)_2$. This apparently gives support to the theory of Irving and Edgington.

An Analytical Experiment

The determination of europium by extraction into a mixture of HTTA and a neutral donor and subsequent measurement of the fluorescence of the organic phase has been found to be an extremely sensitive method of analysis. Nikolaeva and Bozheval'nov (78) have found the extraction of $Eu(TTA)_3$(1,10-phenanthroline) into benzene and subsequent measurement of the fluorescence to be very useful for the determination of europium in lanthanum oxide. They were able to determine 5×10^{-3} to 5×10^{-4}% europium in La_2O_3. Kononenko et al. (60) have also used the extraction of $Eu(TTA)_3$(1,10-phenanthroline) with benzene and subsequent measurement of the fluorescence of the organic phase to determine europium. They report a detection limit of 0.2 microgram of europium.

The only report of the use of HTTA mixed with an organophosphorus reagent for the fluorometric determination of europium was made by Ballard and Edwards (10), who found the extraction of europium with a mixture of HTTA and TOPO to be useful.

In order to illustrate the high sensitivity of the fluorescence of synergic complexes, an analytical curve for the fluorometric determination of europium that had been extracted into a mixture of HTTA and TOPO in cyclohexane was constructed. The data used in the construction of this curve were obtained by extracting a known amount of europium from 10 milliliters of an acetate buffer with a pH of 5.5 into 10 milliliters of cyclohexane containing 0.1 millimole of HTTA and 0.1 millimole of TOPO. The shaking time was 2.5 hours. After separating the phases and centrifuging the organic phase, the fluorescence of this phase at 617 mμ was measured using an exciting wavelength of 390 mμ. The analytical curve obtained is shown in Figure 24. It is easily seen that the detection limit under the conditions described above is 0.003 microgram of europium per milliliter. This is quite a low limit when one considers that the conditions used were not idealized conditions but practical ones. The concentrations of HTTA and of TOPO were placed at 100 times the highest europium concentration so that the europium could be extracted in the presence of large excesses of other ions without depleting the ligand concentration. The presence of the large excess of HTTA decreases the intensity of the fluorescence by absorbing the exciting light. If the data for Figure 24 had

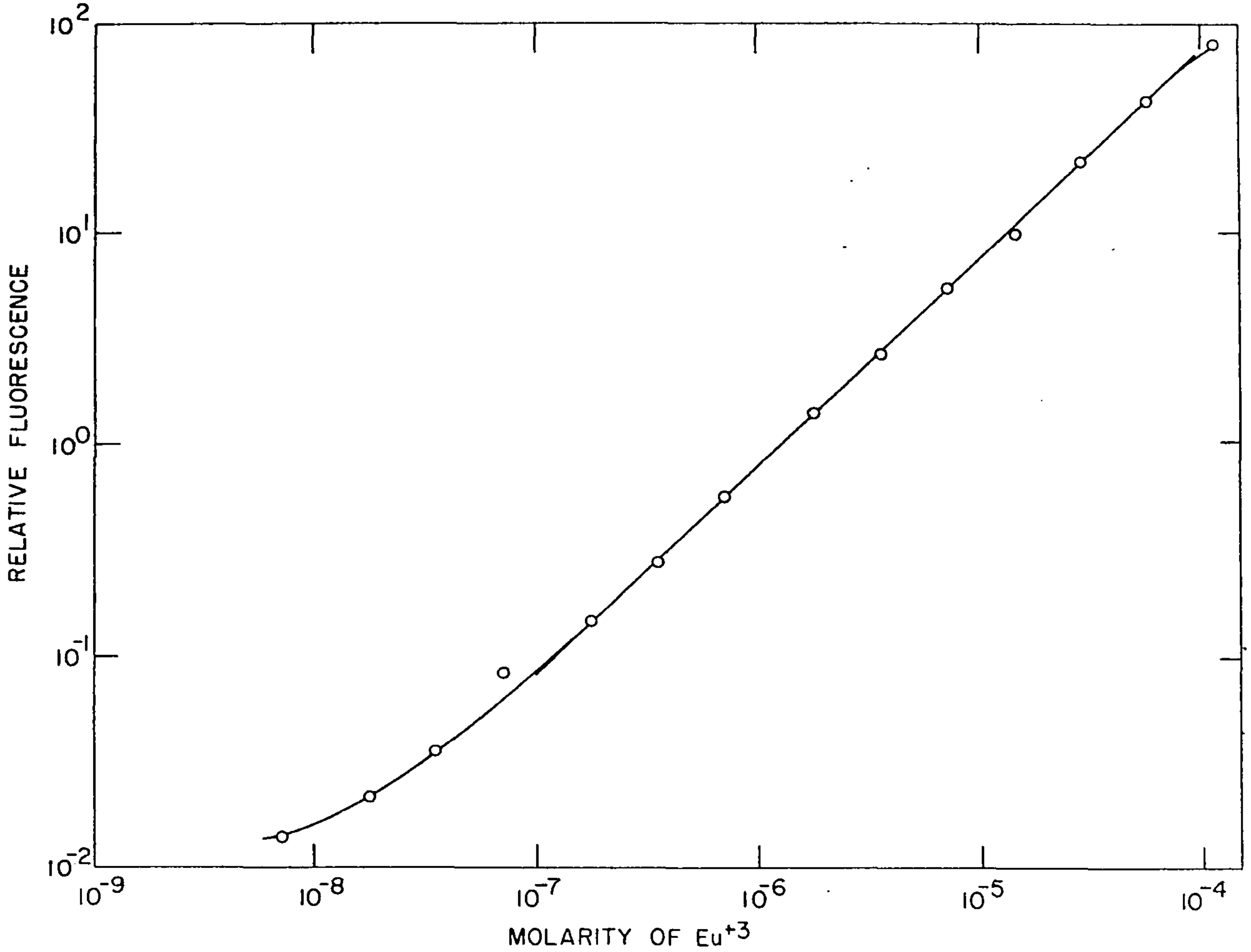


Figure 24. Fluorescence of the organic phase at 617 mμ as a function of the concentration of europium

been collected under less practical conditions, the detection limit would have been several orders of magnitude lower.

The effect of four other metal ions on the fluorescence of europium was tested by adding different known amounts of these ions, before extraction, to the aqueous phase, which contained 1.5 micrograms of europium. The data are compiled in Table 18 and plotted in Figure 25 as relative fluorescence versus the ratio of the concentration of the diverse ion to the concentration of Eu(III). Th(IV) gives a serious negative interference, and Sm(III), which fluoresces at 617 mμ, gives a serious positive interference. Gd(III) gives only a slight negative interference when it is 100 times the Eu(III) present. Yttrium(III) does not interfere, even when it is 200 times the Eu(III) present. It is likely that La(III), Lu(III), and Sc(III) would not interfere and that the other lanthanides would interfere to various extents (106). Therefore, it should be possible to directly determine small amounts of europium(III) in the presence of large amounts of Y(III), Sc(III), La(III), and Lu(III). It should also be feasible to determine small amounts of europium(III) in the presence of those metal ions which interfere to a moderate extent by using the method of additions. Ions such as Ce(IV) and Th(IV) which interfere very seriously would probably have to be separated from the europium.

Table 18. Effect of diverse ions on the fluorescence of Eu^{+3} extracted into a mixture of HTTA and TOPO

Diverse ion	$\frac{[\text{Diverse ion}]}{[Eu^{+3}]}$	Relative fluorescence
Y^{+3}	175	0.84
	87.5	0.76
	43.8	0.81
Gd^{+3}	218	0.72
	109	0.76
	54.5	0.80
Sm^{+3}	9.76	1.11
	4.88	0.86
Th^{+4}	186	0.20
	93.0	0.29
	46.5	0.45
	9.30	0.68

Conditions: $[Eu^{+3}] = 1.00 \times 10^{-6}$

$pH = 5.5$

Relative fluorescence 0.795 ± 0.006[a]

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[a] The result of five determinations in the absence of diverse ions.

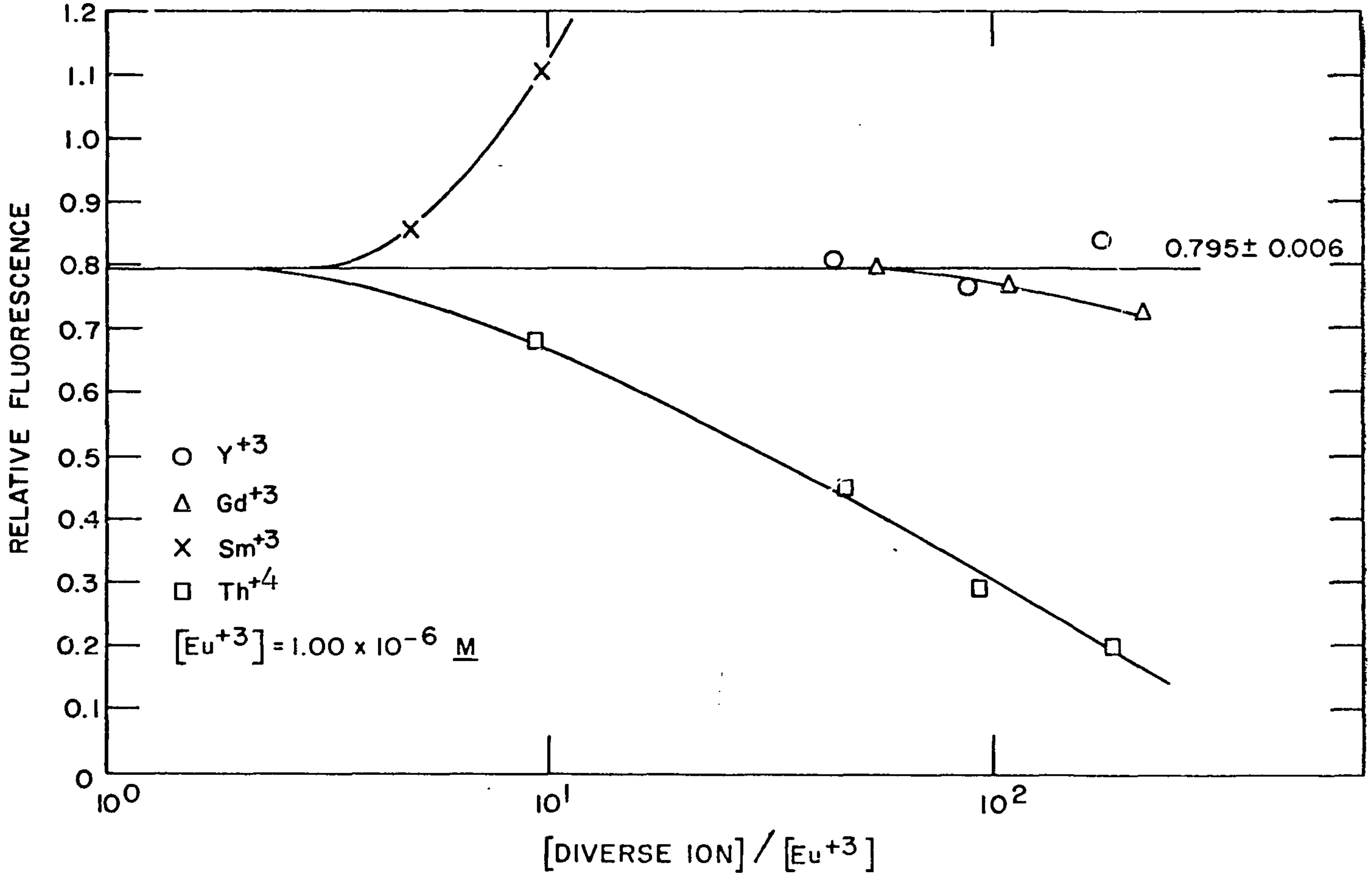

Figure 25. The effect of diverse metal ions on the fluorescence of europium

SUMMARY

An extensive review of synergic solvent extraction is given, including a review of the explanations that have been proposed for the phenomenon of synergism.

The solvent extraction of tracer europium(III) from chloride medium ($\mu = 0.1$) into mixtures of thenoyltrifluoroacetone (HTTA) with methylenebis(di-n-hexylphosphine oxide), MHDPO; trimethylenebis(di-n-hexylphosphine oxide), PHDPO; tetramethylenebis(di-n-hexylphosphine oxide), BHDPO; or tri-n-octylphosphine oxide, TOPO, in cyclohexane was studied. The dependence of the distribution ratio on pH, on $[HTTA]_o$, and on the concentration of the neutral organophosphorus compound was determined by an application of the law of mass action. The europium-containing species in the organic phase were shown to be $Eu(TTA)_3(TOPO)_2$, $Eu(TTA)_3(MHDPO)$, $Eu(TTA)_3(PHDPO)$, and $Eu(TTA)_3(BHDPO)$. The equilibrium constants for the formation of the above complexes were calculated, and it was found that the stabilities of the adducts of $Eu(TTA)_3$ with the diphosphine oxides increase in the order MHDPO < PHDPO < BHDPO.

A molar ratio study of the extraction of europium(III) from an acetate buffer with a pH of 5.5 was used to confirm the composition of the complexes listed above and to show the

formation of $Eu(TTA)_3(TOPO)$ as well. The formation of $Eu(TTA)_3(TOPO)$ was confirmed by a loading capacity study and by a fluorometric molar ratio study.

The solvent extraction of tracer europium(III) from perchlorate medium ($\mu = 0.1$) into mixtures of HTTA with TOPO or MHDPO in cyclohexane was studied. The law of mass action was applied to both of these systems. The variables pH, $[HTTA]_o$, $[TTA^-]$, and $[TOPO]_o$ were considered in the first system, and the variables pH, $[HTTA]_o$, $[MHDPO]_o$, and $[ClO_4^-]$ were considered in the second system. The method of continuous variations was applied to the system containing MHDPO. The europium-containing species in the organic phase were shown to be $Eu(TTA)_3(TOPO)_2$ and $Eu(TTA)(MHDPO)_3(ClO_4)_2$. In the latter case the loss of chelation energy due to the replacement of two TTA ligands has been compensated by the formation of a more stable complex containing three stable rings with bidentate MHDPO. Equilibrium constants for the formation of the above two complexes were calculated. Table 19 is a compilation of all of the equilibrium constants that were determined for the complexes formed in the various systems.

The solvent extraction of tracer europium(III) from perchlorate medium ($\mu = 0.1$) into mixtures of HTTA and MHDPO

Table 19. Summary of the equilibrium constants

System	Constants
Eu(III), Cl^-/HTTA, TOPO	$\log K^*_{3,2} = 7.58$
	$\log \beta^o_{3,2} = 13.41$
Eu(III), ClO_4^-/HTTA, TOPO	$\log K^*_{3,2} = 8.11$
	$\log \beta^o_{3,2} = 13.94$
Eu(III), Cl^-/HTTA, MHDPO	$\log K^*_{3,1} = 5.01, 5.09, 4.95$
	$\log \beta^o_{3,1} = 10.84, 10.92, 10.78$
Eu(III), Cl^-/HTTA, PHDPO	$\log K^*_{3,1} = 5.32$
	$\log \beta^o_{3,1} = 11.15$
Eu(III), Cl^-/HTTA, BHDPO	$\log K^*_{3,1} = 5.91$
	$\log \beta^o_{3,1} = 11.74$
Eu(III), ClO_4^-/HTTA, MHDPO	$\log K^*_{1,2,3} = 14.14, 14.18$
Eu(III), ClO_4^- or Cl^-/HTTA	$\log K^*_{3,0} = -5.83$

in 1,2-dichlorobenzene was also studied. Application of the law of mass action and the method of continuous variations indicated that under most conditions more than one complex is extracted and that the composition of the predominant mixed ligand complex is probably dependent on these conditions.

All of the bifunctional phosphine oxides are thought to be bidentate in the complexes found here, and europium(III) is apparently octa-coordinate in each complex.

The analytical usefulness of the fluorescence of mixed ligand complexes of europium with TTA and neutral organophosphorus compounds is illustrated.

SUGGESTIONS FOR FUTURE WORK

The preparation of solid synergic complexes with several bifunctional phosphine oxides and several monofunctional neutral donors should be attempted. Differential thermal analysis of these complexes should provide information on the strength of the bond that the neutral donor forms with the chelate. This information would provide a basis for deciding whether the neutral donor is bonded to the chelate by direct coordination to the metal or by hydrogen bonding to the TTA moiety of the molecule. A nmr study of solutions of the isolated complexes should provide information that would allow one to decide whether the phosphoryl groups of the bifunctional phosphine oxides are equivalent or not.

A detailed kinetic study of the solvent extraction process might provide information that would indicate the order in which the ligands are added to the metal. Healy (40) made a brief study that seemed to indicate that the synergic effect is caused by the action of the neutral donor on the TTA-metal complex; however, his study was far too brief to allow a definite conclusion.

Values of the formation constants of the complexes of metal ions with TTA in aqueous solution are needed as an aid in the interpretation of solvent extraction data obtained for mixed ligand systems. These constants would also be useful in the calculation of equilibrium constants for the formation of the mixed complexes.

It was pointed out in LITERATURE REVIEW that some of the synergic solvent extraction systems studied by Irving and Edgington probably should be restudied, because their data are subject to question in some cases. For example, in their study of the extraction of Th(IV) from nitrate medium into mixtures of HTTA and TBPO in cyclohexane (53), the concentration of Th(IV) in the organic phase was often greater than the ligand concentration.

Healy (40,41) found that the complexes of the heavy lanthanides with TTA tend to form only monosolvates with TOPO. The light lanthanides, however, tend to form primarily disolvates. It was noted earlier in RESULTS AND DISCUSSION that there are significant differences in the equilibrium constants for the formation of the mixed complexes of Pm(III), Eu(III), and Tm(III). This behavior has been attributed to steric hindrance in the complexes of the heavy lanthanides (65). It would be of interest to investigate the possibility of separating the lanthanides by solvent extraction with a mixture of HTTA and MHDPO. The stability of the adducts and, therefore, the synergic enhancement should decrease with increasing atomic number of the lanthanides. An adduct former with bulky side groups such as methylenebis(di-2-ethylhexylphosphine oxide) or methylenebis(di-2-ethylbutylphosphine oxide) might prove even more useful, because the effects of steric hindrance on the formation of the adduct would be even more important.

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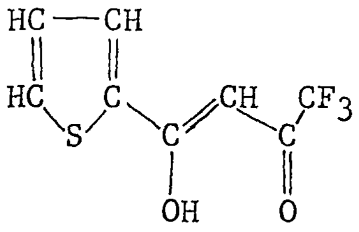
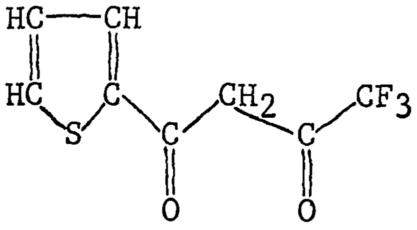
APPENDIX

4,4,4-trifluoro-1-(2-thienyl)-1,3-butanedione (thenoyltrifluoroacetone)

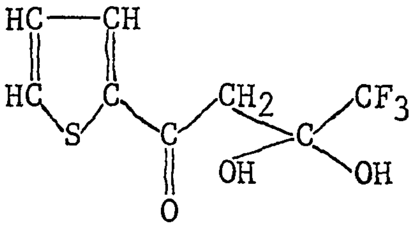
HTTA



Enol form



Keto form



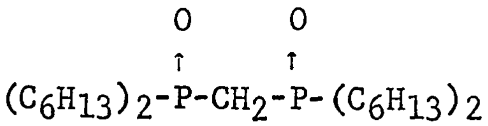
Ketohydrate form

Tri-n-octylphosphine oxide

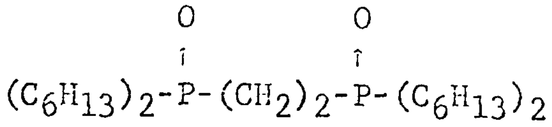
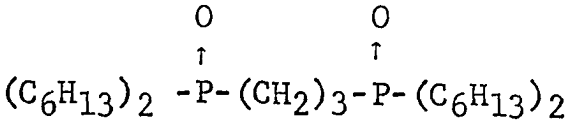
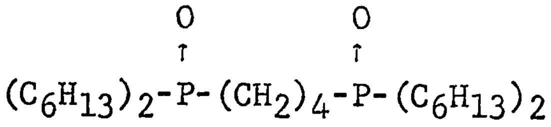
TOPO $(C_8H_{17})_3\text{-P}\rightarrow O$

Methylenebis(di-n-hexylphosphine oxide)

MHDPO



$(C_6H_{13})_2\text{-}\overset{\overset{O}{\uparrow}}{P}\text{-}CH_2\text{-}\overset{\overset{O}{\uparrow}}{P}\text{-}(C_6H_{13})_2$

Dimethylenebis(di-*n*-hexylphosphine oxide)	EHDPO	 $(C_6H_{13})_2-\overset{\overset{O}{\uparrow}}{P}-(CH_2)_2-\overset{\overset{O}{\uparrow}}{P}-(C_6H_{13})_2$
Trimethylenebis(di-*n*-hexylphosphine oxide)	PHDPO	 $(C_6H_{13})_2-\overset{\overset{O}{\uparrow}}{P}-(CH_2)_3-\overset{\overset{O}{\uparrow}}{P}-(C_6H_{13})_2$
Tetramethylenebis(di-*n*-hexylphosphine oxide)	BHDPO	 $(C_6H_{13})_2-\overset{\overset{O}{\uparrow}}{P}-(CH_2)_4-\overset{\overset{O}{\uparrow}}{P}-(C_6H_{13})_2$

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