1964

Solvent extraction properties of some bis(di-n-hexylphosphinyl) alkanes

John Edward Mrochek
Iowa State University

Recommended Citation

Mrochek, John Edward, "Solvent extraction properties of some bis(di-n-hexylphosphinyl) alkanes " (1964). *Retrospective Theses and Dissertations*. 3003.
https://lib.dr.iastate.edu/rtd/3003

MROCHEK, John Edward, 1933–
SOLVENT EXTRACTION PROPERTIES OF SOME
BIS(DI-*n*-HEXYLPHOSPHINYL)ALKANES.

Iowa State University of Science and Technology
Ph.D., 1964
Chemistry, analytical

University Microfilms, Inc., Ann Arbor, Michigan

SOLVENT EXTRACTION PROPERTIES OF SOME BIS(DI-<u>n</u>-HEXYLPHOSPHINYL)ALKANES

by

John Edward Mrochek

A Dissertation Submitted to the
Graduate Faculty in Partial Fulfillment of
The Requirements for the Degree of
DOCTOR OF PHILOSOPHY

Major Subject: Analytical Chemistry

Approved:

Signature was redacted for privacy.

In Charge of Major Work

Signature was redacted for privacy.

Head of Major Department

Signature was redacted for privacy.

Dean of Graduate College

Iowa State University
Of Science and Technology
Ames, Iowa

1964

TABLE OF CONTENTS

TABLE OF CONTENTS
(Continued)

TABLE OF CONTENTS
(Continued)

INTRODUCTION

Separation from each other and subsequent analytical determination of the 102 known chemical elements is a formidable task for the present-day analytical chemist. Quantitative determinations of the components of complex mixtures composed of widely varying amounts of various elements are the rule rather than the exception in industries of the twentieth century atomic and space ages. Certain specialized instrumental methods such as X-ray fluorescence and emission spectrography are effective in the determination of certain elements without the necessity of elaborate separation schemes. However, despite the availability of these modern more discriminating methods of measurement, successful solutions to many analytical problems still depend heavily on separation processes. Thus the analytical chemist is usually faced with a two-fold problem; separation of the desired constituent followed by measurement of the amount present by the best available method.

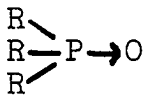
Developments in separation processes have not kept pace with developments in the field of quantitative measurements. It is only relatively recent work in the fields of ion exchange, density gradient elution, solvent extraction and the various chromatographic methods (thin-layer, reversed-phase, vapor-phase and liquid-phase) that has helped to close the gap between separations of complex mixtures and analytical measurement of their individual constituents.

Solvent extraction maintains a distinct advantage in the analytical separations field because of its simplicity, speed and wide scope of applicability (26, 69, 70). Applicable to both trace and macro levels of concentration and utilizing apparatus no more complicated than a separatory funnel, solvent extraction techniques enjoy a distinct advantage over the classical precipitation method of separation. Usually cleaner separations can be achieved by the use of a two-phase solvent extraction system because of the advantage gained by elimination of the coprecipitation problems usually present in classical gravimetric methods.

The discovery of the nuclear fission properties of plutonium 239 in 1941 (95) led to greatly expanded research and development in non-precipitation methods of separation. Although it had been recognized early in the Plutonium Project that precipitation processes were not the most efficient or economic methods, major research in the development of non-precipitation processes was delayed until near the end of and immediately after World War II. This was the period when solvent extraction entered the atomic energy program. The first two solvent extraction processes to be developed were the Redox Process using hexone (methyl isobutyl ketone) and the TTA Process using both hexone and TTA (thenoyltrifluoroacetone) (95). From about 1945 onward, the search for solvent extractants was vigorously pursued in the United States, England, Canada, France and the U. S. S. R.

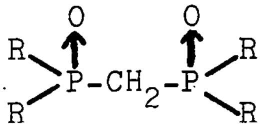
Organophosphorus compounds made their debut in the atomic energy program with a classified report in 1945 reporting the use of TBP (tributyl phosphate) as a solvent extractant. This work was later declassified and reported in the regular literature in 1949 (112).

In recent years the use of long chain amines and various organophosphorus compounds as solvent extractants has been studied extensively. A considerable amount of research reported in the literature has been devoted to comparisons of various structural types of neutral organophosphorus reagents. These compounds have the general formula



where the R may be an alkyl, aryl or an alkoxy group. When all three substituents are alkyl or aryl groups, the compound is a phosphine oxide. With the successive substitution of alkyl or aryl groups by one, two or three alkoxy groups, a phosphinate, phosphonate and finally a phosphate is obtained. These neutral molecules solvate metal salts or the hydronium ion by coordination with the phosphoryl oxygen (56, 115), probably displacing one or more water molecules from the coordination sphere of the hydrated ion and forming a more hydrophobic species. The resulting complex is readily extracted into an organic phase provided the alkyl groups are sufficiently large. The solvent extraction system characterized by the reaction of a metal salt with these neutral organic molecules is known as a ion association system.

One of the problems encountered with the use of the neutral organophosphorus compounds in analytical separations is their lack of specificity. Members of the staff of the Ames Laboratory (Ames, Iowa) attempted to build this quality into organophosphorus reagents by synthesizing compounds with a structure somewhat analogous to a β-diketone. The general formula for these compounds is



where the R groups are alkyl (branched chain, straight chain or cyclic) or aryl. This type of structure might possibly undergo enolization and ion size differentiation might also occur through the formation of a six-membered chelate ring with the metal.

The first in a series of these compounds was bis(di-*n*-hexylphosphinyl)methane (HDPM) synthesized by Richard and others (89). This bidentate ligand exhibited certain differences in solvent extraction behavior when it was compared to the monodentate ligand tri-*n*-octyl phosphine oxide (TOPO) (71, 76). HDPM generally appeared to be a more powerful extractant than TOPO and, in the case of extraction from perchlorate media, the distribution coefficients, $K_d = \frac{(C_m)_o}{(C_m)_a}$, were often several orders of magnitude larger. Comparative viscosity studies in low dielectric media revealed another difference between the two compounds. HDPM appeared to form polymers whereas TOPO remained monomeric when carbon tetrachloride solutions of the two reagents were saturated with uranium(VI) nitrate (71). This work posed an interesting and thought-provoking problem involving investigation of the interaction between solvent and solute in ion association solvent extraction systems composed of bidentate organophosphorus solvents and metal salt solutes.

Two possibilities exist for the reaction of a bidentate ligand with a metal ion such as uranium. Discrete complex formation may occur with one or more molecules of the ligand each coordinated through one or two phosphoryl oxygens to the metal ion. If the coordination positions of the metal can be saturated by the ligand alone, an ion pair may be formed in the organic phase. If the ligand is sterically hindered or somehow otherwise prevented from saturating the coordination positions of the metal, either the anions or water molecules may fill the coordination sphere. The second possibility is either chain polymers or a interlaced network of polymeric species. To preclude the latter possibility, it was planned to choose organic diluents of sufficiently high dielectric constant to prevent polymer formation if possible.

The method chosen to investigate the complexation of metals by bidentate organophosphorus compounds involved the syntheses of compounds with identical alkyl substituents on the phosphorus atom but with increasing separation between the two coordinating phosphoryl groups of the molecule. Compounds were synthesized with two (HDPE), three (HDPP) and four (HDPB) carbon chain bridges between the di-*n*-hexylphosphinyl groups (see APPENDIX for complete nomenclature). It was planned to study these compounds under identical conditions and compare them to HDPM and then to utilize the data to postulate the mechanism of interaction between solvent and solute in these systems.

After completion of initial comparative solvent extraction studies, it was realized that more comprehensive data would be required before the mechanism of interaction for neutral bidentate organophosphorus compounds with metal salts could be postulated. To accomplish this end the emphasis of the investigation was shifted to the field of infrared spectroscopy. Changes induced in the infrared spectra of organophosphorus compound-metal salt mixtures by varying the ligand/metal ratio were utilized to help explain the solvent-solute interactions.

Uranium(VI) nitrate was the metal salt chosen for most of the solvent-solute investigations because it exhibits relatively strong interaction with organophosphorus compounds. A second important reason for choosing this particular metal salt was the fact that valuable information about the coordination of the anion could be gained by observation of the effect of ligand/metal ratio on the infrared spectra of the nitrate anion.

The interpretation of the infrared data indicated that displacement of the anion from the coordination sphere of the metal salt was occuring and this led to another important phase of investigation, the measurement of molar conductance. Conductivity measurements and viscosity studies were correlated with infrared spectral data and ultimately led to the postulation of a mechanism for the reaction of bidentate organophosphorus compounds with uranium(VI) nitrate.

The reaction of the monodentate ligand, TOPO, with uranium(VI) nitrate was selected as a basis for many of the conclusions postulated for the bidentate ligand-uranium(VI) nitrate systems. During the course of these investigations, two previously unreported complexes of TOPO and uranium were observed.

REVIEW OF THE LITERATURE

The work reported in this thesis is mainly concerned with studies of neutral organophosphorus reagents. This review will, therefore, only cover the literature pertinent to neutral organophosphorus solvent extraction systems.

Monodentate Organophosphorus Solvent Extraction Systems

Tributyl phosphate (TBP)

The first reported use of TBP as a solvent extractant was described by Warf (112) who, in the course of a search for a solvent which was not oxidized by cerium(IV) nitrate, discovered the solvent extraction properties of this important organophosphorus reagent. The original work, done in connection with the Plutonium Project, was reported in the classified literature in 1945.

The influence of diluent on the extraction of nitrates by TBP is of both practical and theoretical importance. The literature is somewhat controversial as to the theoretical effect of diluent on solvent extraction properties. Komarov and Shuvanlov (62) found that variations in distribution coefficients of uranium(VI) nitrate could not be predicted on the basis of diluent polarity. Taube (104) pointed out that extraction depends on the interaction between the complex and permanent or induced dipoles in the diluent and on the work which is needed to form a "hole" in the organic phase. Siekierski (100) believed that the effect of diluent on extraction was restricted to weak dipole-dipole interactions. He expected a strong diluent effect when either the extractant or the extracted complex was strongly polar, or either one of them interacted with molecules of the diluent by specific chemical forces such as hydrogen bonds.

Nitric acid extraction by TBP has been extensively studied by many authors (3, 60, 105, 107) and it is now taken as established that the main extracted species is anhydrous $TBP \cdot HNO_3$ over a considerable range of nitric acid and TBP concentrations. Infrared spectral evidence indicates strong hydrogen bond formation between the phosphoryl oxygen and nitric acid (60, 79, 86).

Several workers have reported infrared evidence for the complex $TBP \cdot H_2O$ (3, 56, 79). Determination of the variation in water content of the organic phase with varying aqueous nitric acid concentration has shown that a minimum was attained at a point where the stoichiometry in the organic phase corresponded to the formation of the 1:1 $TBP \cdot HNO_3$ complex (60). This minimum was identified with the displacement of water from the $TBP \cdot H_2O$ species by nitric acid. Beyond this point, the amount of water in the organic phase increased with increasing aqueous nitric acid concentration. No general agreement appears to have been reached as to the reason for this increase in the amount of water in the organic phase.

Nitric acid in excess of that required for the 1:1 $TBP \cdot HNO_3$ complex is present in the organic phase when equilibrations are conducted with aqueous acid solutions of greater than 7 M concentration. The nature of the interaction between TBP and this excess acid is uncertain. The views range from that of Collopy and others (20, 21) that undissociated nitric acid is distributed between the aqueous and the organic (composed of $TBP \cdot HNO_3$) phases through that of Tuck (105, 106) that hydrated nitric acid adds to the ester R-O-P bond, or that of Hardy and others (38), that it adds to the oxygens of the nitrate group. Recent infrared evidence presented by Kinney (60) seems to rule out addition to the nitrate or the ester oxygens. Thus, it seems established that excess nitric acid together with water dissolves in $TBP \cdot HNO_3$ but, because of the possibility of there being many specie present, there is no agreement on whether this is simple dissolution, or whether definite complexes are formed.

Whitney and Diamond (115) reported that perchloric and perrhenic acid formed the ion pair complex, $3TBP \cdot H_3O^+ \cdot yH_2O$ -------ClO_4^- or ReO_4^-, in the presence of excess TBP($0 \leq y \leq 1$). The proposed structure has one TBP molecule hydrogen bonded to each of the hydrogens of the hydronium ion.

General compilations of data from inorganic extraction studies with the $TBP \cdot HNO_3$ system have been published (32, 50) and much more information is available for this system than for others such as perchloric or hydrochloric acids. This lack of information is probably due to complications introduced into the system by partial hydrolysis (hydrochloric or perchloric acid catalyzed) of TBP producing acid esters (58, 59). These acidic impurities may react synergistically to produce distribution ratios much higher than could be obtained with either TBP or the impurity alone (6).

A considerable amount of research has been devoted to the solvent extraction of lanthanide nitrates by TBP (42, 85, 94). Nickolaev and Sorakina (77) reported that distribution data for the lanthanide nitrates may be misleading because of a self-salting-out effect and also the opposite effect, self-salting-in. Some interesting separations were achieved by the use of solvent-swollen polymers in gel-liquid extraction systems (102). An important advantage of this type of system is the elimination of entrainment losses which often occur in solvent-solvent systems. Siekierski and Fidelis (101) were very successful in separations of small amounts of lanthanides by the use of reversed-phase partition chromatography with TBP used as the stationary phase and concentrated nitric acid used as the eluting agent (101).

The trivalent actinide elements were found to resemble the trivalent lanthanide nitrates in their extraction by TBP if one compared elements with the same ionic radii (9). This seemed to indicate that ionic radius was the controlling factor in solvent extraction systems. It was found that the tetravalent actinide nitrates were strongly extracted with extraction generally increasing in the order Th<Np(IV)<Pu(IV) while the hexavalent actinides, which were also strongly complexed, exhibited a reversed trend, Pu(VI)<Np(VI)<U(VI) (2).

Ishimori and others (51) reported the extraction behavior of about 50 chemical elements from hydrochloric acid media. Comparison of their data with anion exchange data of Kraus and Nelson (65) appeared to indicate similarity in the mechanisms of distribution for the solvent extraction and anion exchange systems (51).

Siekierski (99) discussed the extraction of several metal salts from perchloric acid with TBP. He found that distribution ratios rose steadily with increasing acid concentration. Several authors have discussed the partition of uranium(VI) perchlorate from a mechanistic point of view (43, 74, 96).

Other monodentate types

There was early recognition of the fact that the solvent extraction properties of TBP depended mainly upon the basiscity (electron donor ability) of the phosphoryl group. Burger (18) found that electronegative substituents such as the phenyl group or chlorine depressed solvent extraction properties tremendously. He also reported that varying the size of the alkoxy groups has very little effect upon the extraction properties of the complex even though it might be expected that this would affect its solubility.

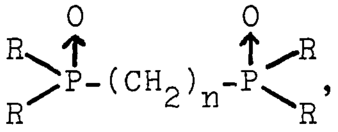
An increase in solubility and viscosity, a decrease in density and a decrease in the stretching frequency of the phosphorus-oxygen bond were noted on passing from phosphate to phosphinate to phosphine oxide. The affinities of these compounds for uranium(VI), plutonium(IV) and plutonium(VI) nitrates were found to increase in the same order (18). In fact, a linear relationship was shown between distribution ratios and phosphoryl bond frequencies (19).

Nomura and Hara (78), studying the effects of branching of the alkyl chain, found a definite increase in distribution ratios for the branched chain phosphates when they compared them to the straight chain types. As would be expected, they found the effect of branching was greatest for substitution at the carbon atom closest to the alkoxy oxygen. Highly branched tricyclohexyl phosphate showed unusually high partition coefficients for uranium.

The knowledge that improved solvent extraction properties were associated with increased alkyl substitution around the phosphorus atom naturally led to more thorough investigations of the group of neutral organophosphorus compounds known as trialkyl phosphine oxides. Blake and others (14) reported the synthesis, physical properties and initial solvent extraction studies of tri-n-octyl phosphine oxide (TOPO) in 1955. Since this initial work, workers have reported that many useful separations are possible with this reagent. White and Ross (114) have published a comprehensive survey of the solvent extractant properties of TOPO for most of the elements of the periodic table from nitrate, chloride, sulfate, phosphate and perchlorate media. They reported that perchlorate systems were not attractive for analytical separations because the metal-perchlorate adducts were less soluble in low dielectric media than those of the other mineral acids. Ishimori and others (49) studied the partition of about sixty elements between aqueous hydrochloric (nitric) acid systems and toluene solutions of TOPO.

Bidentate Organophosphorus Solvent Extraction Systems

Organophosphorus compounds with the structure,



were mentioned as possible solvent extractants for uranium(VI) in a classified report in 1952 (15). A proposed synthesis of the compound with n = 2 was described. The authors postulated that a seven-membered chelate ring could be formed with the uranyl ion coordinated to both phosphoryl oxygens. They also postulated a compound with a methylene bridge (n = 1) which could form a six-membered ring. No further work was reported on compounds with this type of structure until 1959 when Healy and Kennedy (39) reported studies on two structurally similar compounds with alkoxy groups attached to phosphorus and n = 1 and 2.

Richard and others (89) first reported the synthesis of the bidentate ligand with a methylene bridge and alkyl substitution around the phosphorus atom in 1960. The compound was gem-bis-(di-n-hexylphosphinyl)methane (HDPM). The solvent extraction properties of this compound for uranium have been studied by the author and others (71). O'Laughlin (81) graphically depicts the extraction properties of HDPM for a large number of elements from perchloric acid media.

Saisho studied the extraction of inorganic nitrates with tetra-n-butyl ethylenediphosphonate (91, 92). He found this compound useful in the separation of some of the lanthanides from zirconium at low acid concentrations.

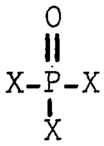
Irani and Moedritzer (47) have studied the acidity constants and the complexing of calcium and magnesium by monomethylene and polymethylene diphosphonic acids. They studied acids with methylene bridges ranging from one to ten carbons in length and found that as n increased, the effect of the two end phosphonic acid groups on each other decreased and became negligible for n larger than three. Complexing of calcium and magnesium was also found to drop off sharply as n increased.

Recently, Siddall has studied the extraction properties of tetraalkyl methylenediphosphonates with varying methylene carbon bridge lengths. He reported that these compounds were powerful chelating extractants for cerium, promethium and americium nitrates (98). He showed that the work of Healy and Kennedy (39), in which they reported that these bidentate organophosphorus compounds were poor solvent extractants, was probably in error.

Nature of the Metal Complexes

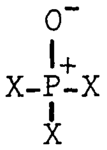
Phosphorus-oxygen bond

The nature of the phosphorus-oxygen bond in quadruply bonded phosphorus compounds has been reviewed by Larsson (66). He concluded that there was no unambiguous evidence of the nature of the P-O bond from observations of physical and chemical properties of compounds containing this entity. All conclusions about this bond were based upon empirical comparisons or arguments of analogy and seemed to favor a resonance hybrid structure encompassing I and II as extremes.



$$\begin{array}{c} O \\ \| \\ X-P-X \\ | \\ X \end{array}$$

I



$$\begin{array}{c} O^- \\ | \\ X-\overset{+}{P}-X \\ | \\ X \end{array}$$

II

In compounds with strongly electron-withdrawing substituents, Structure I is most important while the trialkyl phosphine oxides are probably best represented by a structure intermediate between I and II with the latter being the most important.

Daasch and Smith (24) have assigned characteristic frequency ranges for a number of molecular groups attached to phosphorus. They assigned the region 1170-1310 cm^{-1} to the vibrations of the phosphoryl group. This is in agreement with the assignment reported by Gore (37).

Cotton and others (22) studied the effect of complex formation on the P-O stretching frequencies of phosphine oxide-transition metal complexes. They concluded that the decrease in this frequency on complexation was due to a decrease in $p\pi \rightarrow d\pi$ back-bonding between oxygen and phosphorus. Nadig (73) has recorded the infrared spectra of TBP and TOPO complexes of many metal nitrates. He obtained an approximately linear correlation between the ionic potential (charge/ionic radius) and the phosphoryl band frequency shift. He regarded this as confirmatory evidence for the interpretation of $\Delta\nu$ (phosphoryl band shift) as indicative of complex strength.

Oshima (84) reported that the metal ions fall into two different groups when plotting the phosphoryl band shift for TBP against the distribution ratio. The lanthanide, actinide and alkaline earth elements form one group called the rare gas type electronic configuration and the transition elements form another called the incomplete d-shell group. He concluded that the electronic configurations of metals in these two groups have different interactions with the solvent on complexing and thus form two different groups in extraction behavior.

The state of the anion

Details of the nature and characteristics of the interaction between cations and anions have always been vague. Part of the difficulty has been due to the barrier of the classical theoretical conception of the interaction as being purely electrostatic between point charges (57). Another hindrance to increased knowledge of these interactions has been the fact that most of these studies have been conducted in water with its special ionizing and solvating characteristics. Increased use of low dielectric, organic solvents has made it possible to demonstrate characteristic alterations of the absorption spectrum of the nitrate ion (55) and of other anions due to their interactions with cations.

The theoretical interpretations of the infrared spectra of many polyatomic groupings have been worked out by application of symmetry properties and group theory methods. Herzberg (41) has related the infrared spectrum of the nitrate ion to the vibrations of a planar triangular configuration of D_{3h} point group symmetry and assigned the frequencies as shown in Table 1. Brand and Cawthon (16) have examined the spectra of liquid and gaseous methyl nitrate in which the nitrato group is strongly bonded to carbon, and made the assignments as illustrated in Table 2. A lowering of symmetry occurs when the nitrate ion (D_{3h} symmetry) is coordinated through the oxygen

Table 1. Infrared band assignments for D_{3h} nitrates

Infrared activity	Notation (NO_3^-)	cm^{-1}	Assignment
inactive	ν_1	1050	N-O stretch
active	ν_2	831	NO_2 deformation
active	ν_3	1390	NO_2 asym. stretch
active	ν_4	720	planar rock

Table 2. Infrared assignments for C_{2v} nitrate in methyl nitrate (liquid)

Infrared activity	Notation ($O-NO_2$)	cm^{-1}	Assignment
active	ν_4	1634	NO_2 asym. stretch
active	ν_1	1282	NO_2 sym. stretch
active	ν_2	859	N-O stretch
active	ν_6	759	non-planar rock
active	ν_5	662	planar rock
active	ν_3	577	NO_2 deformation

(C_{2v} symmetry) to the carbon atom (41). The doubly degenerate ν_3 frequency in the symmetrical nitrate ion undergoes a splitting into ν_4 and ν_1 in the strong covalently bonded nitrato group of methyl nitrate. In addition, ν_2, usually inactive in the infrared for the nitrate ion is observed. Ferraro (30) has labeled the difference $(\nu_4 - \nu_1)$ as Δ.

Increasing splitting values, $\Delta(\nu_4 - \nu_1)$, were observed on going from monovalent to tetravalent metallic nitrates. In addition, it was observed that the $\Delta(\nu_4 - \nu_1)$ values were linearly related to the ionic potential of the metal. These data were interpreted as indicating that the degree of splitting of ν_4 and ν_1 was a measure of the polarization of the anion or, in other words, the amount of covalent character in the metal-to-nitrate bond (31). This was in agreement with the postulation by Fajan (27) that the smaller the size and/or the greater the charge of a cation the greater the induced distortion or polarization of the anion. The splitting observed for methyl nitrate, 352 cm^{-1} (Table 2), and that observed for an ionic nitrate like sodium nitrate, 0 cm^{-1} (57), present two extremes which can be utilized as standards in the interpretation of the infrared spectra of nitrates.

Ferraro (30) compared the infrared spectra of TBP-metal solvates with their corresponding metal hydrates and found that the nitrate groups have a higher degree of covalency in the TBP solvates. Gatehouse and others (36) have examined the spectra of a number of metal nitrates and assigned regions of absorbance for the various frequencies of the covalently bonded nitrato group (Table 3).

Table 3. Infrared assignments for C_{2v} nitrates

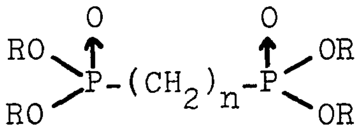
Infrared activity	Notation ($O-NO_2$)	cm^{-1}	Assignment
active	ν_4	1531-1481	NO_2 asym. stretch
active	ν_1	1290-1253	NO_2 sym. stretch
active	ν_2	1034-970	N-O stretch
active	ν_6	800-781	non-planar rock
active	ν_5	not obs.	planar rock
active	ν_3	not obs.	NO_2 deformation

Stoichiometry of complexes

The stoichiometry of the metal complexes formed with neutral organophosphorus compounds has been investigated by many workers. The trivalent lanthanide elements are generally regarded as forming trisolvates with TBP (30, 94). Slopes of logarithmic plots of distribution ratios versus uncomplexed solvent concentration presented by some authors (85, 99) seem to indicate lower complexes but non-ideal solutions (44) or absence of a correction for the reduction in free ligand concentration by complexation with acid can explain these data.

Solvent extraction studies with the actinide nitrates have indicated varying degrees of solvation by neutral organophosphorus reagents. Siddall (97) postulated the formation of disolvates and trisolvates of thorium and dialkyl alkylphosphonates.

He found the trisolvate to be the most prevalent species in agreement with work reported by Madigan and others (68). He also reported that branched chain alkyl groups depressed the formation of the disolvated complex. These data may indicate that steric hindrance prevents close approach of the solvating molecules and thus, with less overlap of orbitals, a greater number are required to effectively solvate the thorium ion. Hexavalent uranium has been reported to form a disolvate with TBP and TOPO from nitrate media (3, 14, 40). Very few reports of monosolvated complexes with monodentate organophosphorus compounds have appeared in the literature. Feder and others (28) have reported such a complex for the TBP-uranium(VI) nitrate system with an equilibrium constant of 2.7. Solovkin and Konorev (103) reported a monosolvate for diisopentyl methyl phosphonate and uranium(VI) nitrate. In addition to the monosolvate, these workers also reported disolvate formations for these systems (28, 103). Healy and Kennedy (39) reported a disolvate and postulated a polymeric species, $[UO_2(NO_3)_2 \cdot S]_n$, for bidentate extractants with the structure,



,

with n = 1 and 2. They did not cite any experimental evidence for their postulation of polymer formation other than some preliminary viscosity studies. Siddall (98) has recently proposed that bidentate ligands with this same general structure are powerful chelating reagents for cerium, promethium and americium nitrates. In contrast to the work of Healy and Kennedy, Siddall (98) postulated that they functioned as bidentate ligands with the formation of discrete complexes rather than polymers.

There was some difference of opinion as to the nature of the uranium(VI) perchlorate-TBP complex. Hesford and McKay (43) reported a disolvate while Naito and Suzuki (74), using infrared spectroscopy, reported a tetrasolvate. The data of Hesford and McKay were based on the logarithmic dependance of K_d(U) on solvent concentration. The aqueous phase contained 10-12 M perchloric acid however, and thus their data probably were not an indication of the actual solvation number because of the large reduction in uncomplexed TBP concentration by complexation with acid.

Vdovenko and others (110) have reported that an anionic complex, $H(UO_2Cl_3)$, is extracted into 100% TBP. The visible spectrum of this trichlorouranyl ion exhibits the same characteristics as that reported for the trinitrouranyl complex by Kaplan and others (54). The existence of this anionic chloride complex leads one to doubt the report by Banerjea and Tripathi (7) stating that the only complex present in solution for chloride/uranium ratios $\leq$ 1000 was the monochloro complex of uranium(VI), $(UO_2Cl)^{+1}$. Vdovenko and others (108) also reported that TBP formed disolvated and trisolvated complexes with uranium(VI) chloride with the former being the most stable complex.

APPARATUS AND REAGENTS

Infrared spectra were obtained with a Beckman, Model IR-7, spectrophotometer equipped with a sodium chloride prism and a dry air purging device. The wavenumber scale was calibrated against atmospheric air and carbon dioxide. The estimated accuracy for the spectral region of interest in this investigation was ± 2 cm^{-1}. Connecticut Instrument Corporation matched, fixed-thickness cells supplied with Irtran-2 windows, separated by teflon (0.1 mm) spacers, were utilized in all infrared spectral measurements of nitrate solutions. The Irtran-2 windows were polished with 600 mesh ground glass to eliminate optical problems caused by the large difference in index of refraction of the windows as compared to that of the organic solutions. Spectral measurements in the visible region were made with a Beckman, Model DU, or a Cary, Model 14, spectrophotometer. A Beckman, Model G, pH meter was used for all pH measurements. Glass-stoppered 30-milliliter separatory funnels equipped with teflon stopcocks, a Burrell wrist-action shaker and a International, Model CL, centrifuge were utilized in partition studies. A Sargent-Malmstadt spectro-electro titrator equipped with a Sargent constant-rate buret was used for the lanthanide partition studies. A remote control Schöniger oxygen flask unit was utilized in the elemental analysis of phosphorus. Carbon and hydrogen were determined using the method and apparatus described by Lysyj and Zarembo

(67) with the additional comment that a Vycor combustion tube was used.

Conductivity measurements were made by Dr. Jerome W. O'Laughlin using a bridge described in his thesis (81). The conductivity cell was a commercial model with a cell constant of approximately 0.01. The cell was stoppered to prevent loss of diluent by volatilization during temperature equilibration.

The lanthanide salts used during the course of this investigation were prepared from the oxides which were Ames Laboratory stock. Primary standard grade potasium nitrate was used in the partition studies for adjustment of ionic strength. The various uranium(VI) salts were prepared by dissolving U_3O_8 in nitric or perchloric acids and then fuming down to rid the salts of excess acid. Uranium(VI)chloride was prepared by dissolution of U_3O_8 in nitric acid followed by repeatedly fuming down with hydrochloric acid; a small amount of formic acid was added to rid the solution of the last traces of nitrate.

The commercially available chromogenic reagent, arsenazo, was purified according to the procedure of Fritz and Johnson-Richard (35). Chlorophosphonazo III, [2,7-bis(4-chloro-2-phosphonobenzeneazo)-1,8-dihydroxynaphthalene-3,6-disulfonic acid] used in the spectrophotometric determination of uranium (75) was synthesized in this laboratory according to procedures given in the literature (29, 75).

Tetra-<u>n</u>-butyl ammonium hydroxide, the non-aqueous base used in the acid extraction studies, was prepared by the method of Fritz and Hammond (34) with one slight change. The mixture of tetra-n-butyl ammonium iodide and silver oxide was agitated in ice water rather than at room temperature. Thymolphthalein, a Harleco reagent, was dissolved in tributylphosphate (0.1%) and served as the indicator for non-aqueous titrations of acids.

The diluent used in infrared studies was 1,2-dichloroethane, a Fisher Certified reagent, and it was used without further purification. The diluent used in partition studies, 1,2-dichlorobenzene, an Eastman Organic Chemical product, was purified by passage through a five foot basic alumina column. Nitrobenzene, the diluent used in the conductivity and viscosity studies, was a "J. T. Baker purified" reagent having a specific conductance of 2.41 x 10^{-8} ohm^{-1} cm^{-1} at 25° C. It was used without further purification.

Tri-n-octyl phosphine oxide, an Eastman Organic Chemicals product, was used without further purification. Bis(di-n-hexylphosphinyl)methane was synthesized in this laboratory by Mr. John J. Richard. The synthesis, purification and analysis were reported in the literature (89). The syntheses, purification and analytical data of all other organophosphorus compounds used during the course of this investigation are reported in the EXPERIMENTAL section.

EXPERIMENTAL

Synthetic Procedures

Synthesis of bidentate organophosphorus compounds

1,2-bis(di-n-hexylphosphinyl)ethane (HDPE), 1,3-bis(di-n-hexylphosphinyl)propane (HDPP) and 1,4-bis(di-n-hexylphosphinyl) butane (HDPB) were synthesized by the procedure reported by Kosolapoff and Struck (63) with one important modification; the excess Grignard reagent was hydrolyzed with 25% sulphuric acid instead of alcoholic potassium hydroxide. This step increased the yields from the reactions to 60-70% compared to the 30-40% yields reported by the above authors. Evidently a considerable amount of their reaction yield was trapped and lost in the magnesium hydroxide filter cake.

The procedure for synthesis of ethylene or trimethylene di-toluene-p-sulfonate, the starting materials used in the previously mentioned syntheses of HDPE and HDPP, is described below.

Procedure A mixture of 2.3 moles of p-toluenesulfonyl chloride and 10 moles of dry pyridine is cooled in a ice bath. One mole of the appropriate diol(ethylene glycol or 1,3-propane diol) is added slowly while maintaining the temperature near 0° C. The reaction is allowed to proceed in the ice bath for four to five hours and then it is removed from the bath and stirred at room temperature for eight hours. The reaction mixture is poured onto crushed ice and the resulting precipitate filtered and washed with ice water. The product is recrystallized from acetone-alcohol solution.

(Acetone added in small amounts to increase the solubility of the di-tosylate in ethanol.)

Ethylene di-p-toluene sulfonate-M.P. 126-27° C. Trimethylene di-p-toluene sulfonate-M.P. 90-92° C.

HDPB was prepared by the method of Kosolapoff and Struck except for the substitution of 1,4-dibromobutane for the corresponding di-tosylate. HDPB and HDPP were purified by recrystallization from petroleum ether while HDPE was recrystallized from acetone.

Physical properties and analytical data The physical properties and analytical data for the three bidentate organophosphorus compounds are reported in Table 4.

Table 4. Physical properties and analytical data for HDPE, HDPP and HDPB

	HDPE	HDPP	HDPB
molecular weight	462.684	476.710	490.738
melting point, °C	161.5-162	106.5-107.5	112.5-113.5
boiling point, °C, mm Hg	246-48, 0.15	250, 0.1	255-58, 0.13
% C, found	67.55	68.04	68.60
theory	67.49	68.03	68.53
% H, found	12.22	12.24	12.26
theory	12.20	12.26	12.32
% P, found	13.3	13.0	12.6
theory	13.39	13.00	12.63

The solubility of HDPM, HDPE, HDPP and HDPB in water at various temperatures has been determined by other workers at this laboratory (82). The data (Fig. 1) show an inverse temperature-solubility relationship similar to that reported for TBP (46) and tributyl phosphine oxide (45). The solubility and melting point of HDPE are considerably different than the other members of the series. No explanation can be advanced for this difference but it may be noted that Kosolapoff and Struck (63) reported a melting point of 174-175° C for 1,2-bis(di-*n*-butylphosphinyl)ethane, a compound which differs from HDPE only in the length of the alkyl groups.

Analytical Procedures

Special notes on analytical procedures

During the investigation of the various analytical methods used during the course of this work, certain shortcomings were noted in some of the existing methods. These are discussed in the following paragraphs.

Carbon and hydrogen analysis The regular combustion tube packing of $CuO-PbCrO_4$ was found to be unsuitable for the determination of carbon in organophosphorus compounds. Low results obtained by this method were thought to be caused by the trapping of carbon by phosphorus pentoxide. A silver permanganate packing was found to give satisfactory results for phosphorus-containing compounds (67). An improvement in

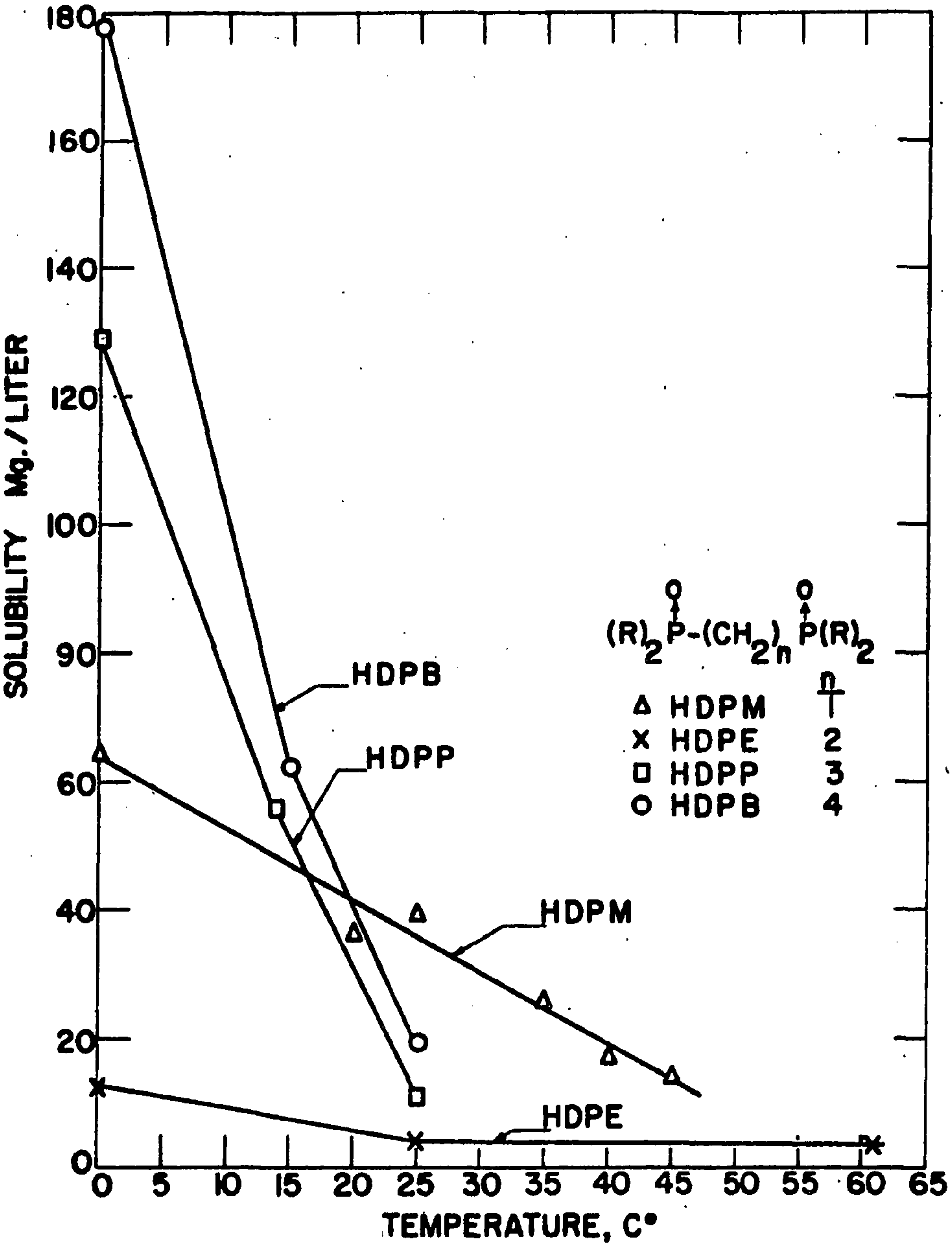


Figure 1. Solubility of bidentate organophosphorus compounds in water as a function of temperature

the mechanical properties of this catalyst may be achieved when its decomposition is conducted at 90-95° C for 24 hours (61).

The catalyst must not be compacted in the combustion tube because this causes holdup of the gaseous combustion products and subsequent low results. Strong heating of the area of the combustion tube from the platinum sample boat up to and including the first silver wire packing was necessary to assure complete combustion of the bidentate organophosphorus compounds. The tube was heated from above and below by means of a Fischer burner and a welding torch.

Phosphorus analysis Elemental analysis of organophosphorus compounds for phosphorus was accomplished by oxidation in a Schöniger flask followed by spectrophotometric measurement of the phosphomolybdivanado complex according to the procedure of Barney and others (8). A 1000-milliliter Schöniger flask was used and it was found that a sample size of 30 milligrams or less was necessary to insure complete combustion. The complex may be read at either one of two wavelengths depending upon the amount present. The molar absorptivities were found to be 3482 liter/mole-cm at 391 mμ and 673 liter/mole-cm at 464 mμ.

Uranium analysis The arsenazo method of analysis (35) was found to be unsuitable for the trace analysis of uranium when it was necessary to destroy excess acid in the sample.

Phosphate, produced by oxidation of the partially water-soluble organophosphorus reagent, introduced variable positive absorbance errors into the method. Perchlorate salts, at very low levels of uranium concentration, also caused positive errors.

Chlorophosphonazo III, first prepared by Nemodruk and others (75), was found to be a very useful reagent for the determination of microgram quantities of uranium. One disadvantage of this reagent is the positive absorbance error introduced by the use of sodium, potassium or ammonium salts (29). The standard curve (0 to 15 µg/25 ml) was displaced upward an average of 0.015 absorbance unit in the presence of 0.06 M potassium nitrate. No effect was noted in the presence of 0.003 M solutions of the same salt. No change in the standard curve was noted on varying the pH of color development over the range 0.4 to 1.0. No buffering was necessary, the blank and sample were adjusted to approximately the same pH with hydrochloric acid and the absorbance read on a spectrophotometer at 670 mµ. The molar absorptivity was found to be 7.83 x 10^4 liter/mole-cm and compared favorably with value 7.86 x 10^4 reported in the literature (75).

The peroxide method, adequately discussed by Sandell (93), was used in the determination of larger amounts of uranium (> 1.5 mg).

Water analysis   Determination of water in the organic phase was accomplished by titration with Karl Fischer reagent utilizing a "dead stop" endpoint detection system (33). The following procedure was used to prepare a titrant with a titer of 3.4 mg H_2O/ml.

Procedure Resublimed iodine (76.2 grams) and 240 milliliters of pyridine (0.07% H_2O) were shaken together for 10 minutes. Absolute methanol (600 ml, 0.03% H_2O) (111) was added and the solution was cooled to near 0° C. Sulfur dioxide (40.5 ml) was added rapidly to the cold solution and the mixture was allowed to stand at room temperature for 24 hours before use.

The titrant was standardized by titration of known volumes of water and checked by titration of weighed amounts of sodium tartrate dihydrate (15.66 ± 0.05% H_2O).

Determination of distribution ratios

Partition data for uranium were obtained by equilibrating a known amount of the appropriate uranium(VI) salt with a known concentration of the organophosphorus reagent in 1,2-dichlorobenzene. Solutions were allowed to equilibrate for 15 minutes at room temperature ($23 \pm 3^\circ$ C) using a wrist-action shaker. After phase separation the metal-poor phase was drawn off, centrifuged and an appropriate aliquot taken for analysis. If analysis of the organic phase was necessary, it was performed by back-extraction with sodium carbonate followed by analysis utilizing the peroxide method.

Determination of the stoichiometries of the higher complexes necessitated appraisal of the solvation number by means of the slopes of logarithmic plots of the distribution ratio, $K_d(U)$, versus equilibrium solvent concentration. This was accomplished by equilibrating trace amounts of uranium(VI) nitrate ($U = 5 \times 10^{-5}$ $\underline{M}$) with varying concentrations of the organic solvents in the inert diluent, 1,2-dichlorobenzene. These organic solutions were protected from light because it was noted that the diluent decomposed slowly, with the formation of acidic products, when it was exposed to light over a long period of time. No detectable extraction of uranium by the diluent alone was observed if its purification was performed as outlined previously and the above precaution observed. Analysis of the aqueous phase was accomplished by means of the arsenazo or chlorophosphonazo III methods as appropriate.

Loading studies were performed by equilibration of a dilute (usually 0.01 $\underline{M}$) solution of the organophosphorus solvent in either 1,2-dichlorobenzene or 1,2-dichloroethane with the perchlorate or nitrate salt of uranium(VI). Solid uranium (VI) salts as well as aqueous solutions (~1 $\underline{M}$) were used. Equilibrations were conducted for varying time periods of from 24 to 120 hours. Visual evidence of light-induced reduction of U(VI) was observed thus it was necessary to protect solutions from exposure to light during equilibrations.

Partition data for the lanthanide elements praseodymium, neodymium, samarium and thulium from hydrochloric, nitric and perchloric acids were obtained by EDTA titration (113) of the aqueous phase before and after equilibration with the organophosphorus solvent extractant. A 3:1 ligand/metal ratio was arbitrarily selected with 0.05 M solvent in 1,2-dichlorobenzene and 0.01667 M lanthanide salt being used. The Sargent-Malmstadt spectro-electro titrator equipped with the approprate filter was used in the photometric detection of all titration endpoints. Indicator blanks were deducted and calculations were made using the number of units (delivery by constant-rate buret, 498 units = 1 ml) of titrant before and after extraction to calculate distribution ratios.

Investigations of acid partition were conducted by equilibrating 10-milliliter portions of 0.05 M organophosphorus reagent in 1,2-dichlorobenzene with an equal volume of aqueous acid of known concentration. An aliquot of the organic phase was withdrawn, diluted with acetone and titrated with tetra-n-butyl ammonium hydroxide in a benzene-methanol mixture to a visual indicator endpoint. The only contribution to the indicator blank was determined to be from the acetone and this was deducted from all titration results. All data were corrected for the extraction of acid by the diluent. Corrections were necessary for 3, 4, 5, 6, 7 and 10 M nitric acid and 10 M hydrochloric acid.

Miscellaneous Procedures

Infrared and visible spectral studies

Solutions were prepared by contacting weighed amounts of $UO_2(NO_3)_2 \cdot 2H_2O$ with eight milliliters of a 0.1 M solution of the organophosphorus compound in 1,2-dichloroethane. The equilibrations were performed in ten-milliliter volumetric flasks at room temperature ($23 \pm 3^\circ$ C) for 24 to 36 hours using a wrist-action shaker. The flasks were wrapped with black tape to protect the solutions from light and thus prevent the photochemical decomposition frequently observed in these systems. They were sealed by wrapping a strip of polyethylene sheet around the glass stopper, inserting it and applying gentle heat to the neck of the flask. After softening the polyethylene, it was allowed to harden under hand pressure. After completion of the equilibrations, the flasks were opened and diluted to volume with 1,2-dichloroethane. The infrared and visible (330-500 mμ) spectra were then recorded on double beam instruments with a matched cell containing diluent placed in the reference beam. These same solutions were then dried with molecular sieves (Linde, 4A) and both spectral regions scanned again and the spectra compared to those of the undried solutions.

All infrared spectra were adjusted to a common baseline in a non-absorbing region of the recorded spectra. A complete series of spectra for one compound were scanned during one day so as to prevent errors due to instrumental fluctuations in day to day operation.

The infrared spectrophotometer was adjusted to 100% transmittance for a scan of diluent versus diluent in the region of the uncomplexed phosphoryl band, thus the reported absorbance of this band is the true absorbance. All other absorbance data are relative to a common baseline since no correction for baseline absorbance was needed.

Per cent transmittance readings were converted to absorbance and plotted versus amount of uranium(VI) nitrate.

Conductivity and viscosity studies

A 0.05 M solution of uranium(VI) nitrate in nitrobenzene was prepared. Using this stock solution and 0.1 M solutions of the individual organophosphorus compounds in the same diluent, solutions containing various ligand/metal ratios were prepared for each individual conductivity measurement. Final uranium concentration was maintained constant at 0.01 M. Conductance data were measured at $25 \pm 0.05^{\circ}$ C.

Ostwald-Fenske type viscometers thermostated at $25 \pm 0.05^{\circ}$ C were used to measure the capillary flow of the uranium (VI) nitrate complexes of HDPM and HDPB in nitrobenzene solution. A capillary was chosen so that the efflux time was always between 100 and 150 seconds. The efflux time of each solution was measured three times; the precision was within 0.5 of a second.

Nuclear magnetic resonance proton spectra

Nuclear magnetic resonance spectra were obtained on a Varian, Model HR-60, high resolution spectrometer. Chemical shifts were measured with respect to tetramethylsilane as an internal reference using side-bands applied by a calibrated audio oscillator.

Samples of the hydrated complexes of HDPM, HDPP, HDPB and TOPO were prepared by equilibrating 0.15 M solutions of the organophosphorus compounds with water. Solutions were allowed to stand for at least 12 hours after equilibration to allow separation of mechanically entrained water.

RESULTS AND DISCUSSION

Extraction of Mineral Acids

The hydrogen ion, as present in strong acids, is unique in its role as the only small, univalent cation to extract appreciably into basic organic solvents. The relatively large distribution ratios for the strongest acids imply that a very specific interaction is taking place between the proton and the solvent, an interaction that does not occur to nearly the same extent for any other cation of comparable (hydrated) size. The proton, being a positive charge concentrated in a very small volume, cannot exist alone in solution, but must coordinate with some electron donor. In a solvent extraction system consisting of a strong acid in aqueous solution and an organic solvent in an inert diluent, the electron donors are the acid anion, water and the basic organic solvent. The extent of extraction depends on the outcome of the competition for the proton among these three solvators.

For strong, completely ionized acids, it can be assumed that the anion is unable to participate in the competition for the proton, and thus its only function is to maintain electrical neutrality. However, since the transfer of the anion from the aqueous phase to the organic phase is subject to the same solvent-solvent and solute-solvent interactions as any other solvent extraction process, the anion has a definite influence on the extent of the extraction. Other effects being equal, large anions of low charge favor extraction into the organic phase. In the absence of other considerations, perchloric acid would be expected to be extracted more completely than hydrochloric or nitric acids. With its large, symmetrical size and diffuse charge, the perchlorate anion is able to exist in the organic phase as a ion pair.

If the anion is a strong enough base to enter into the competition for the proton--i.e., the acid is not completely dissociated in aqueous solution,--an entirely different extraction system is formed. In this case, the extraction takes place through the formation of a hydrogen bond between the basic organic solvent and the undissociated acid, and since the extracting species is essentially a neutral molecule so that no charge transfer across phase boundaries occurs, the distribution ratios are quite high.

The nitrate ion exhibits strong basic tendencies in more concentrated solutions. The concentration of undissociated nitric acid was reported to represent 50% of the total in 9 M acid and 32% of the total in 6.6 M nitric acid (87).

Comparative acid extractions for the four bidentate organophosphorus compounds and TOPO are illustrated in Table 5 and Figures 2, 3 and 4.

Nitric acid, as expected, is extracted to the greatest extent by all five organophosphorus reagents. The extraction

Table 5. Mineral acid extraction data for HDPM, HDPE, HDPP, HDPB, and TOPO

	mmole acid extracted/10 ml.					Ratio, $\frac{(\mathrm{Acid})_o}{(\mathrm{HDPX\ or\ TOPO})_o}$				
	HDPM	HDPE	HDPP	HDPB	TOPO	HDPM	HDPE	HDPP	HDPB	TOPO
$HClO_4$, M										
0.1	0.12	0.21	0.26	0.29	0.12	0.24	0.41	0.52	0.59	0.23
0.5	0.23	0.39	0.44	0.47	0.22	0.46	0.77	0.88	0.94	0.44
1.0	0.27	0.46	0.49	0.50	0.24	0.54	0.93	0.98	1.00	0.49
3.0	0.40	0.52	0.51	0.55	0.29	0.80	1.03	1.02	1.09	0.57
4.0	0.47	0.54	0.54	0.61	0.32	0.94	1.07	1.09	1.21	0.65
5.0	0.52	0.59	0.60	0.68		1.04	1.18	1.21	1.36	
6.0	0.53	0.64	0.71	0.78	0.43	1.07	1.28	1.42	1.56	0.86
7.0	0.58	0.73	0.82	0.87	0.48	1.15	1.46	1.64	1.75	0.96
10.0	0.90	1.01	1.01	1.02	0.52	1.79	2.02	2.02	2.03	1.03
HNO_3, M										
1.0	0.48	0.66	0.70	0.75	0.46	0.96	1.32	1.40	1.50	0.93
3.0	0.91	0.98	0.97	0.98	0.52	1.81	1.96	1.94	1.97	1.04
4.0	0.97	1.02	0.99	1.01	0.53	1.94	2.03	1.99	2.02	1.06
5.0	1.01	1.04	1.03	1.06	0.56	2.03	2.08	2.07	2.13	1.11
6.0	1.03	1.08	1.08	1.11	0.58	2.06	2.16	2.16	2.23	1.17
7.0	1.05	1.13	1.14	1.28	0.64	2.10	2.26	2.29	2.56	1.29
10.0	1.18	1.42	1.52	1.68	0.91	2.35	2.84	3.05	3.36	1.83
HCl, M										
1.0	0.01	0.04	0.06	0.09	0.01	0.02	0.07	0.12	0.17	0.02
3.0	0.11	0.32	0.38	0.44	0.12	0.22	0.64	0.77	0.89	0.24
4.0	0.20	0.47	0.54	0.59	0.22	0.40	0.94	1.09	1.19	0.44
5.0	0.33	0.59	0.69	0.74	0.32	0.66	1.19	1.37	1.48	0.64
6.0	0.45	0.69	0.81	0.84	0.42	0.91	1.38	1.63	1.69	0.84
7.0	0.58	0.78	0.94	0.98	0.53	1.16	1.56	1.89	1.97	1.06
10.0	0.86	1.02	1.31	1.40	0.65	1.71	2.03	2.62	2.79	1.31

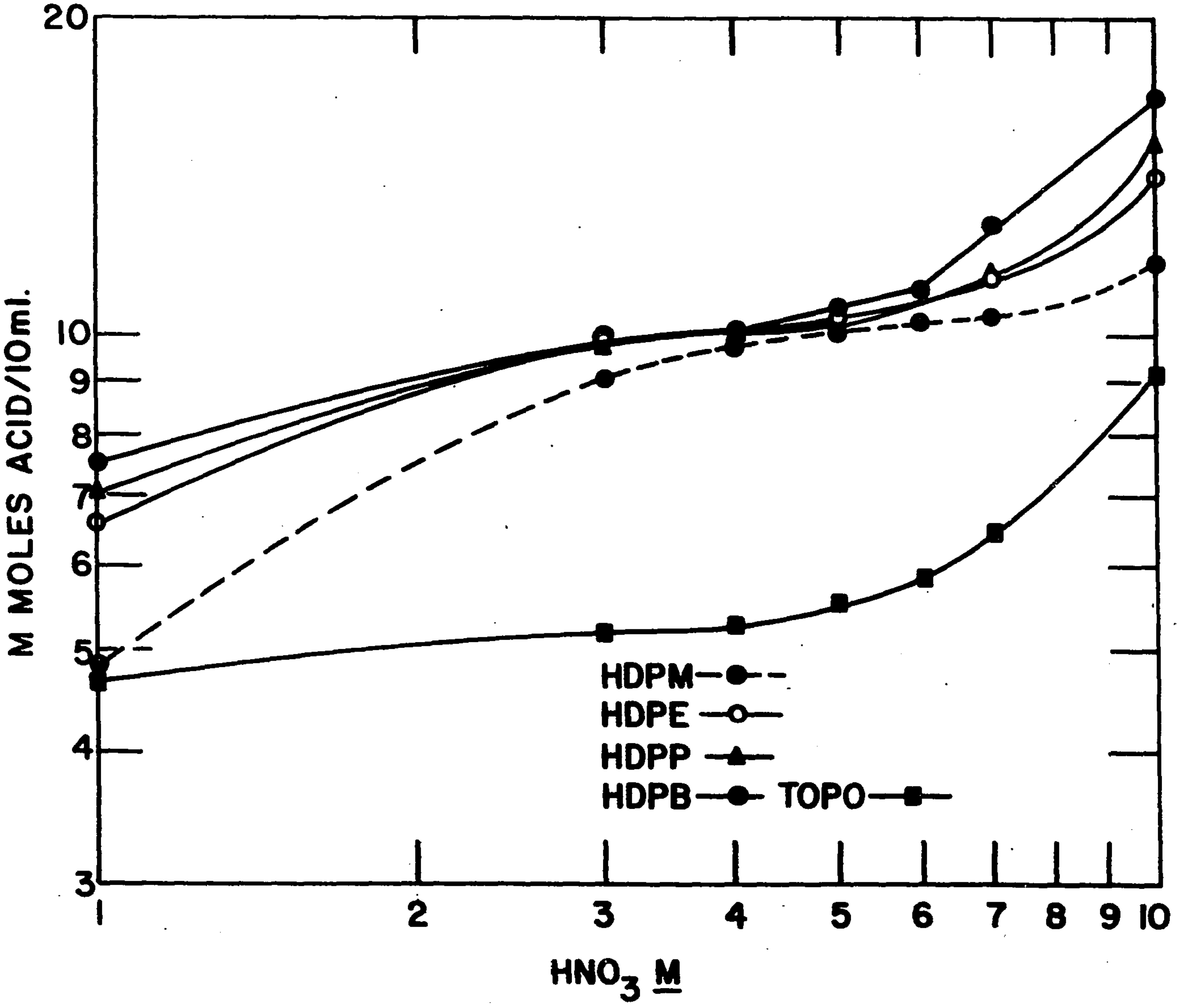
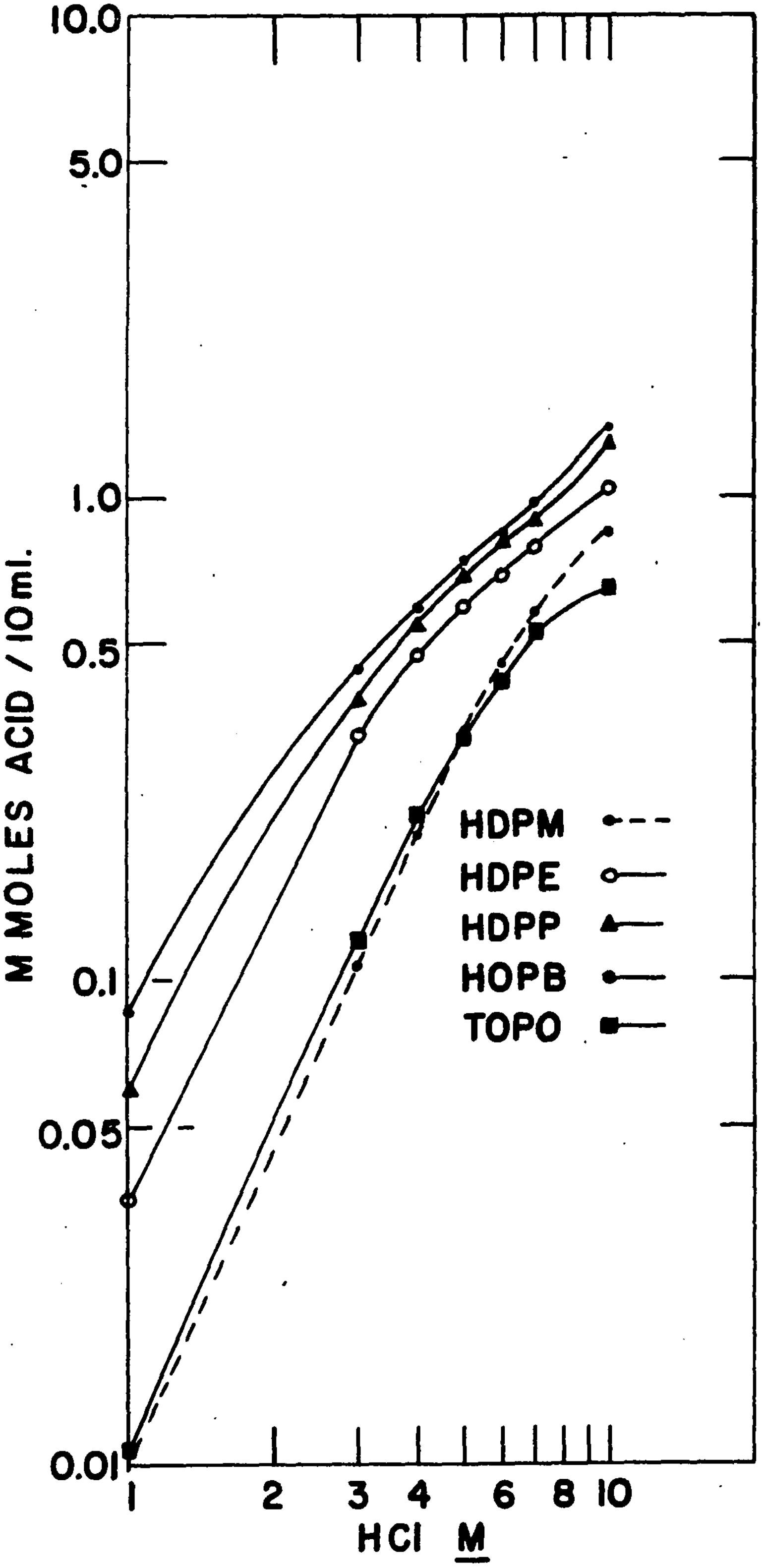


Figure 2. Extraction of nitric acid by 0.05 M organophosphorus compounds (1:1 phase ratio)

Figure 3. Extraction of hydrochloric acid by 0.05 M organophosphorus compounds (1:1 phase ratio)


10.0
5.0
1.0
0.5
0.1
0.05
0.01
M MOLES ACID / 10 ml.
1
2
3
4
6
8
10
HCl M
HDPM
HDPE
HDPP
HOPB
TOPO

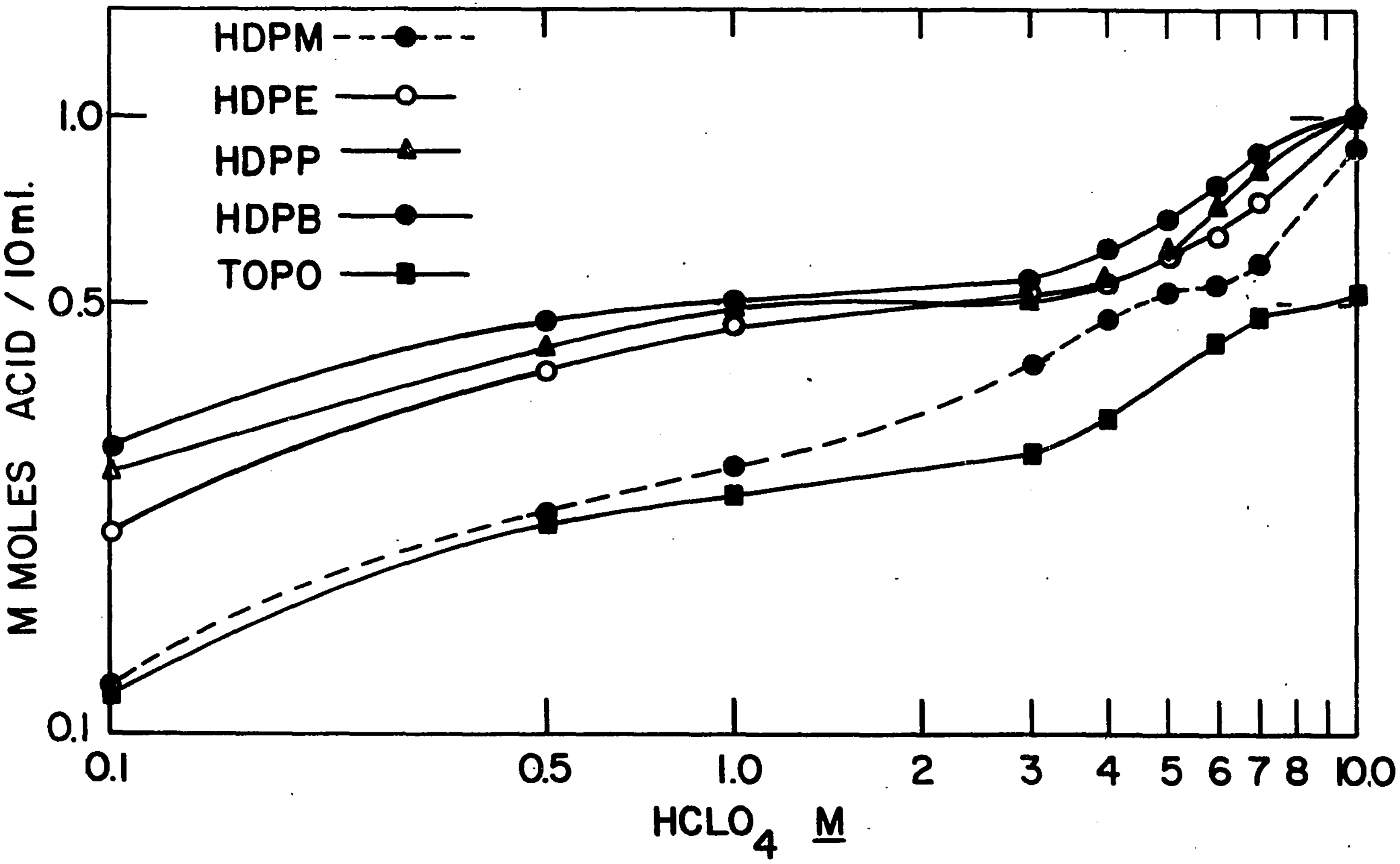


Figure 4. Extraction of perchloric acid by 0.05 M organophosphorus compounds (1:1 phase ratio)

of nitric acid by 1,2-dichlorobenzene (Table 6) seemed to confirm the existence of undissociated nitric acid in aqueous nitric acid solutions. The partition of neutral nitric acid molecules into the organic phase probably explains the relatively high molar ratios, $\frac{[\text{acid}]_o}{[Y]^*_o}$ [1], extracted into the organic phase. In all cases it was considerably more than the stoichiometric amount expected for the reaction of one acid molecule with each phosphoryl oxygen of the molecule. The data of Table 5 have been corrected for the acid extracted by the diluent alone.

The extraction of perchloric acid was generally greater than that of hydrochloric acid for concentrations ranging

Table 6. Extraction of nitric acid by 1,2-dichlorobenzene[a]

HNO_3, <u>M</u>	Acid extracted, mmoles/10 ml.
1	0
3	0.0032
4	0.0080
5	0.0160
6	0.0273
7	0.0450
10	0.1880

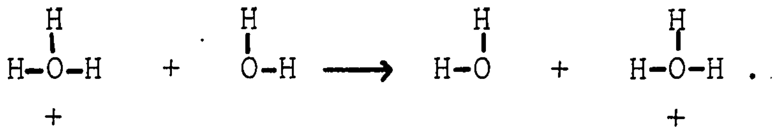
[a] 1:1 phase ratios used in all extractions.

---

[1] Y = HDPM, HDPE, HDPP, HDPB or TOPO and [ ]* refers to initial molar concentration.

from 0.1 to 5 M. Above these concentrations, the extraction of hydrochloric acid was generally greater. Extraction from 10 M hydrochloric acid also produced molar ratios, $\frac{[\text{acid}]_o}{[Y]_o^*}$, stoichiometrically larger than expected but for only HDPP, HDPB and TOPO. The diluent alone extracted 0.042 mmoles/10 ml of hydrochloric acid from the 10 M solution (this correction has been applied to the data of Table 5). No extraction by the diluent alone was observed for the remainder of the hydrochloric acid solutions and all of the perchloric acid solutions.

The reason for the anomalous behavior in the extraction of hydrochloric acid from solutions of higher concentration (> 6 M) cannot be stated with certainty but a possibility may be the presence of undissociated hydrochloric acid at high concentrations. Robinson and Stokes (90) discussed the possibility of hydrogen chloride molecules existing in higher concentrations of acid as an explanation for conductivity data which was considerably lower than theory predicted but they discarded this idea on the basis of low vapor pressure measurements above 4 M hydrochloric acid. They advanced an explanation for the decreased mobility by invoking the proton-jump mechanism,



$$\underset{+}{\mathrm{H{-}\overset{\overset{H}{|}}{O}{-}H}} + \mathrm{\overset{\overset{H}{|}}{O}{-}H} \longrightarrow \mathrm{H{-}\overset{\overset{H}{|}}{O}} + \underset{+}{\mathrm{H{-}\overset{\overset{H}{|}}{O}{-}H}} .$$

At high electrolyte concentrations, a substantial proportion of the water molecules must be oriented around ions in positions which leave them unable to participate in the normal coordinated or "hydrogen-bonded" water structure. Such molecules would presumably not be available as arrival-points for the "jumping" protons thus causing a considerable decrease in the mobility of the proton. This explanation should be applicable to perchloric acid also and thus does not appear to explain the reversal in trend of acid extraction at higher concentrations of hydrochloric and perchloric acids. Activity coefficients also do not shed any light on the situation as they are lower for hydrochloric acid than they are for perchloric acid at higher concentrations (90).

The dialkyl phosphinyl group ($R_2-\overset{\overset{O}{\uparrow}}{P}-$) has been shown to exhibit electronegative inductive effects (88, 89) and thus two of these groups, separated by a single methylene carbon, would be expected to exert mutual inductive effects on each other. This would tend to decrease the availability of electrons on the oxygen for hydrogen-bonding to acid. This mutual inductive effect would be expected to decrease with increasing length of the methylene bridge between the groups. This reasoning was confirmed by the acid extraction data obtained for the four bidentate organophosphorus compounds (Table 5). The compounds were, in order of increasing affinity for acids, HDPM < HDPE < HDPP < HDPB. Another contributing factor to the order observed would be the decreased steric hindrance to extraction due to increased separation between the donor sites of the molecule. TOPO was found to extract the least amount of acid but this is because it has only one site available for coordination.

The extraction of 0.3065 M and 1 M nitric acid solutions by varying concentrations of the organophosphorus extractants was studied to determine equilibrium constants for their reactions with nitric acid. The equilibrium constant for the reaction,

$$Y_{(o)} + H^{+1}_{(a)} + NO_{3\,(a)}^{-1} \longrightarrow Y\cdot HNO_{3(o)} \quad ,$$

is given by Equation 1,

$$K_1 = \frac{K_d(H)}{\left[NO_3^{-1}\right]\left[Y\right]} \tag{1}$$

$$\text{where} \quad K_d(H) = \frac{\left[Y\cdot HNO_3\right]_{(o)}}{\left[\left[HNO_3\right]^{*}_{(a)} - \left[Y\cdot HNO_3\right]_{(o)}\right]} \qquad \text{and}$$

Y = HDPX(X = M, E, P, B) or TOPO. The ratio of acid extracted to bidentate organophosphorus ligand was less than one in all cases with the solution having the lower concentration of acid and thus the only significant species was assumed to be the 1:1 complex. The data and constants are tabulated in Table 7. The equilibrium constants indicate the same order of affinity for the proton as indicated by the extraction data for varying acid concentration solutions.

Table 8 contains the data for extraction from 1 M nitric acid. Equilibrium constants were calculated only for HDPM and TOPO as the ratio of acid in the organic phase/organic solvent, $\frac{[Y \cdot HNO_3]_o}{[Y]_o^*}$, was greater than one for the other compounds. This indicated significant quantities of the diprotonated species were being formed and there was no method of measuring the amount of free ligand.

Partition of Uranium(VI) with HDPM, HDPE, HDPP, HDPB and TOPO

The equilibria involved in the partition of a metal between an aqueous phase and an organic solvent can be very complex and many unsolved problems are involved. In many cases more than one complex species is extracted into the organic phase and thus, for ion association systems, there is no convenient, accurate measure of the amount of uncomplexed ligand in the organic phase. Activity coefficients in the organic phase are usually assumed to be constant although this is not generally true. The role of the so-called "inert" diluent is not at all clearly understood, although in some cases it can

Table 7. K_1 for the extraction of 0.3065 M HNO_3 by HDPM, HDPE, HDPP and HDPB

	$[HDPX]^{*}_{(o)}$	$K_d(H)$	K_1
HDPM	$5x10^{-2}$	0.04241	3.84
	$2x10^{-2}$	0.01583	3.45
	$1x10^{-2}$	0.007203	3.03
	$5x10^{-3}$	0.003309	2.72
		Average	3.26
HDPE	$5x10^{-2}$	0.07915	9.38
	$2.5x10^{-2}$	0.03885	9.36
	$1x10^{-2}$	0.01526	9.23
	$5x10^{-3}$	0.008131	10.49
		Average	9.32
HDPP	$5x10^{-2}$	0.1008	16.51
	$2.5x10^{-2}$	0.04558	16.36
	$1x10^{-2}$	0.01961	16.31
	$5x10^{-3}$	0.009980	16.92
		Average	16.52
HDPB	$5x10^{-2}$	0.1221	26.88
	$2.5x10^{-2}$	0.05994	27.06
	$1x10^{-2}$	0.02345	26.31
	$5x10^{-3}$	0.01131	23.74
		Average	26.00

*Initial molar concentrations.

Table 8. Extraction of 1 M nitric acid by HDPM, HDPE, HDPP, HDPB and TOPO

	$[Y]^*_o$ [a]	$K_d(H)$	Ratio, $\frac{[Acid]_o}{[Y]^*_o}$	K_1
HDPM	5.0×10^{-2}	0.0480	0.909	11.1
	2.0×10^{-2}	0.0193	0.940	16.7
	1.0×10^{-2}	0.00965	0.949	19.3
	5.0×10^{-3}	0.00477	0.943	17.1
	2.5×10^{-3}	0.00232	0.921	11.9
			Average	15.2
HDPE	5.0×10^{-2}	0.0700	1.30	
	1.0×10^{-2}	0.0144	1.40	
	5.0×10^{-3}	0.00724	1.43	
	2.0×10^{-3}	0.00344	1.70	
	1.0×10^{-3}	0.00148	1.47	
HDPP	5.0×10^{-2}	0.0759	1.40	
	2.5×10^{-2}	0.0372	1.42	
	1.0×10^{-2}	0.0157	1.53	
	5.0×10^{-3}	0.00783	1.54	
HDPB	5.0×10^{-2}	0.0819	1.50	
	2.5×10^{-2}	0.0406	1.55	
	1.1×10^{-2}	0.0177	1.58	
	5.5×10^{-3}	0.00868	1.56	
	1.0×10^{-3}	0.00170	1.69	
TOPO	1.0×10^{-1}	0.1028	0.923	14.9
	5.0×10^{-2}	0.0464	0.879	8.1
	1.0×10^{-2}	0.00928	0.910	10.6
	5.0×10^{-3}	0.00443	0.874	7.1
			Average	10.2

[a] $[Y]^*_o$ denotes initial concentration of organophosphorus solvent.

exert an enormous influence on the partition between phases. Regarding the aqueous phase, the general question of the behavior of mixed electrolytes at high concentration remains to be solved. The effects of hydration of ions, particularly anions, needs investigation and the phenomena of salting-out and salting-in have never been adequately explained. The previous factors are merely a partial listing of unsolved problems facing an experimentalist in the field of solvent extraction. These problems have forced scientists to rely upon empirical studies and comparisons to a considerable extent in evaluations of new solvent extractants.

Comparative extractions of uranium(VI) nitrate, chloride and perchlorate were utilized as a means of probing into the interaction of a metal with the four bidentate organophosphorus compounds HDPM, HDPE, HDPP and HDPB. Tri-n-octyl phosphine oxide (TOPO) was chosen as a control compound or, in other words, a basis for some of the conclusions reached about the bidentate ligands. TOPO was chosen for this purpose because, being a monodentate ligand, the nature of its complexes would be more easily understood.

Extraction from nitric acid

The curves for the extraction of uranium(VI) nitrate from varying concentrations of nitric acid appeared to be very similar for all compounds (Figure 5). The compounds were, in order of increasing extraction, TOPO < HDPM < HDPB < HDPP < HDPE

(Table 9). Decreasing distribution ratios with increasing acid concentration appeared to be best explained by the competition of undissociated nitric acid molecules for the active sites of the ligands. The effect of nitrate complexing of uranium in the aqueous phase should not be important because the stability of the mononitrate complex has been reported to be rather low (1, 10, 25).

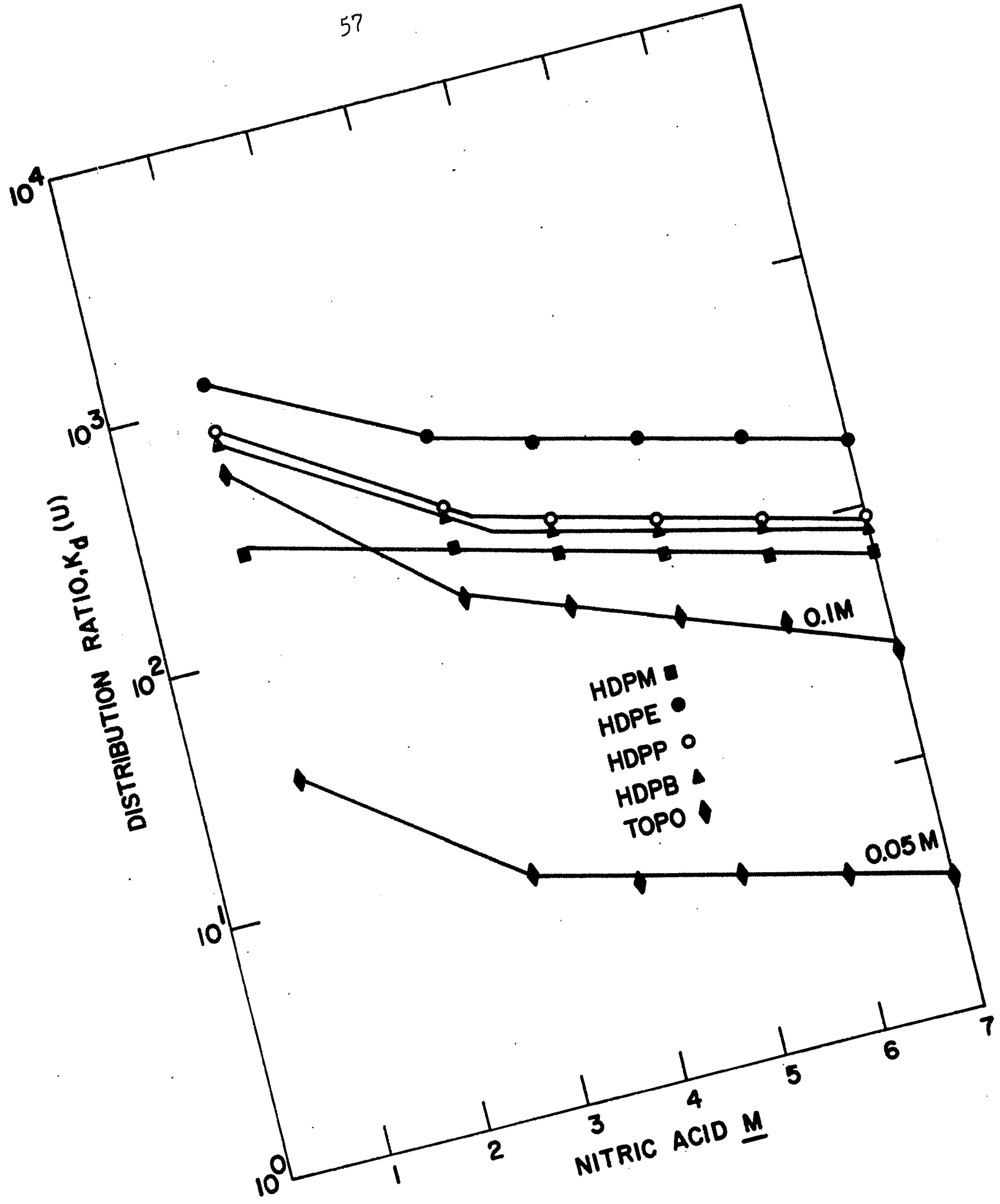
Table 9. Solvent extraction of uranium(VI) nitrate with HDPM, HDPE, HDPP, HDPB and TOPO

	Distribution ratio, $K_d(U)$					
HNO_3, M	HDPM	HDPE	HDPP	HDPB	TOPO	
						a
1	249.8	1189	792	688	31.7	536
3	171.2	472.9	242.5	221.8	8.21	105.6
4	128.3	355.2	175.0	156.5	6.26	78.2
5	100.5	289.8	137.6	125.6	5.31	56.0
6	78.9	235.9	110.0	102.1	4.22	42.5
7	65.5	181.0	94.0	79.9	3.29	26.5

Conditions: organophosphorus compound-0.05 M (unless otherwise indicated)
uranium(VI) nitrate-------0.01667 M
1:1 phase ratio
diluent-1,2-dichlorobenzene

a TOPO-0.1 M

Figure 5. Variations in the distribution ratio of uranium (VI) nitrate with increasing acid concentration at constant ligand concentration (0.05M also 0.1M TOPO) and constant ligand/M (3:1 also 6:1 TOPO)


10^4
10^3
10^2
10^1
10^0
DISTRIBUTION RATIO, K_d (U)
1
2
3
4
5
6
7
NITRIC ACID M
HDPM ■
HDPE ●
HDPP ○
HDPB ▲
TOPO ◆
0.1M
0.05M

Extraction from hydrochloric acid

The partition of uranium(VI) chloride between a aqueous phase and an organic phase consisting of 0.05 M organophosphorus solvent in a diluent was studied as a function of hydrochloric acid concentration. Generally, the extraction curves were quite similar for all five compounds (Figure 6) with very low distribution ratios obtained at 0.1 M acid, rapidly increasing to very high distribution values for the extraction from 5 M HCl. In order of increasing affinity for uranium(VI) chloride (5 M HCl), the compounds were; TOPO < HDPP < HDPB < HDPE < HDPM (Table 10, Figure 6). The rapid increase in distribution ratio with increasing acid concentration was also characteristic of the hydrochloric acid extraction data (Figure 3).

The stability constant of the monochloro complex of uranium(VI) was reported to be approximately four times as great as that of the mononitrate complex (45). This may account for the lower distribution ratios obtained at low acid concentrations of hydrochloric acid as compared to nitric acid. Hydrochloric acid is thought to be completely ionized and thus the competition effect caused by extraction of undissociated acid molecules should be non-existent for this acid as opposed to nitric acid where extensive association occurs (87). The maximum observed at 5 M hydrochloric acid could be due to either one or possibly a combination of two factors; decreasing

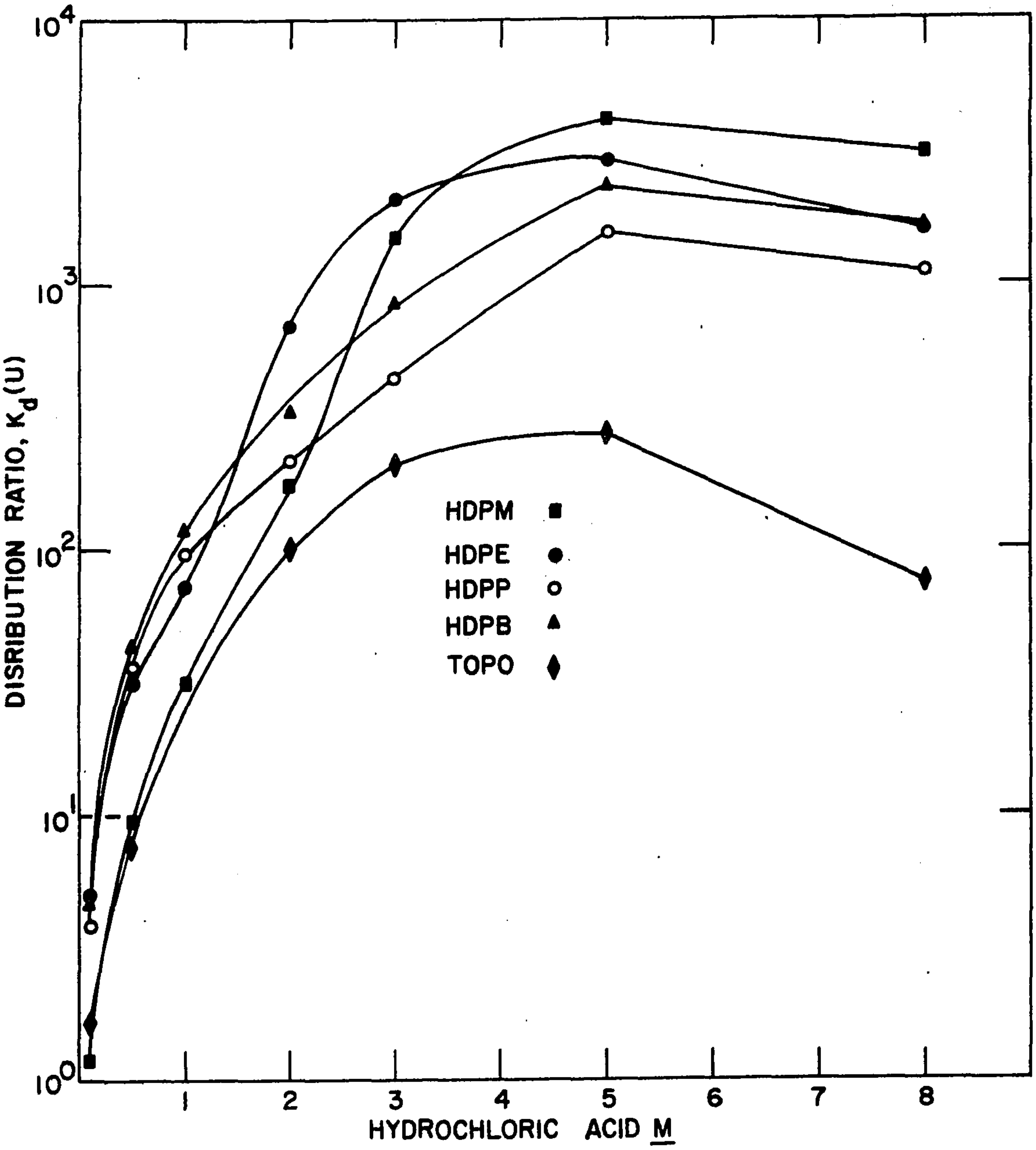


Figure 6. Variations in the distribution ratio of uranium(VI) chloride with increasing acid concentration at constant ligand concentration (0.05M) and constant ligand/M (3:1)

Table 10. Solvent extraction of uranium(VI) chloride with HDPM, HDPE, HDPP, HDPB and TOPO

	Distribution Ratio, $K_d(U)$				
HCl, M	HDPM	HDPE	HDPP	HDPB	TOPO
0.1	1.18	4.92	3.86	4.73	1.66
0.5	9.58	33.3	36.1	43.4	7.90
1	31.8	72.6	96.6	117.5	
2	169.8	694	287.6	328.4	99.5
3	1495	2060	695	843	209.0
5	4180	2910	1550	2330	270.8
8	3260	1590	1100	1680	73.1

Conditions: organophosphorus compound- 0.05 M
uranium(VI) chloride------ 0.01667 M
1:1 phase ratio
diluent- 1,2-dichlorobenzene

activity of water with increasing acid concentration and/or the presence of a neutral dichloro complex of uranium(VI). The presence of a neutral dichloro complex of uranium(VI) would lead to increased distribution ratios because it would be extracted more easily than a positively charged cation. The anion exchange behavior of uranium(VI) chloride makes it seem quite likely that such a neutral complex is formed in higher concentrations of hydrochloric acid (64). Vdovenko and others (109) have reported the presence of the dichloro and anionic trichloro complexes of hexavalent uranium in acetone. They also reported that the latter complex was extracted into 100% TBP (110).

Extraction from perchloric acid

Two factors seem to be of considerable importance in the partition of inorganic salts between water and organic solvents. These factors are differences in free energy of solvation in water and the organic solvent for both the cation and the anion and the complex-forming tendency of the latter.

Since the anion was the only quantity varied during the course of the work reported in this section, the differences in extraction must be due to the difference in anions. Bjerrum (11, 12) has discussed the difference between the free energy of solvation of an ion in two solvents of different dielectric constant. His results indicated that extraction into the organic phase increased with decreasing charge and increasing radius of an ion. This should be particularly true for anions therefore, considering only free energies of solvation, the perchlorates should be capable of being well extracted since the perchlorate ion is large and symmetrical with a small charge. With its symmetry and size favoring delocalization of charge, the perchlorate ion can form ion pairs in the organic phase rather easily. Another factor favoring the extraction of perchlorates is the high activity of its salts in concentrated solution (90). Because of this high activity, the overall free energy change for transfer of the salt from aqueous perchloric acid to the organic phase may be highly negative and as a consequence, extraction may be good. On the other hand, the complex-forming tendency of this anion is very small and if the organic ligand is unable to saturate the coordination positions of the metal ion, water molecules may enter the coordination sphere. This would tend to decrease extraction since it would make the metal ion more hydrophilic, offsetting to some extent the hydrophobic qualities induced by coordination with the organic ligand.

The extractions of uranium(VI) perchlorate by the five organophosphorus compounds fall into three general groups (Figure 7). HDPM and HDPE have very high distribution ratios ($> 10^3$), HDPP and HDPB exhibit intermediate values (generally < 30), while TOPO has a very low affinity for uranium(VI) perchlorate ($K_d < 2$) (Table 11).

Table 12 contains a comparison of the uranium(VI) perchlorate extraction by HDPM and HDPE using different ligand/metal ratios. The data seem to indicate that the species being extracted for these compounds is the disolvated complex. The possibility of a trisolvated complex being the principal species would seem to be ruled out by the data since even a small reduction in ligand concentration by complexation with acid would be sufficient to cause a significant drop in the distribution ratio. The partition data obtained for 3:1 ligand/metal ratios (Table 12) represent greater than 99.9% extraction of uranium. A monosolvated complex was ruled out by saturation studies (Table 13) using 1 <u>M</u> aqueous uranium(VI)

Figure 7. Variations in the distribution ratio of uranium (VI) perchlorate with increasing acid concentration at constant ligand concentration (0.05M also 0.1M TOPO) and constant ligand/M(3:1 also 6:1 TOPO)

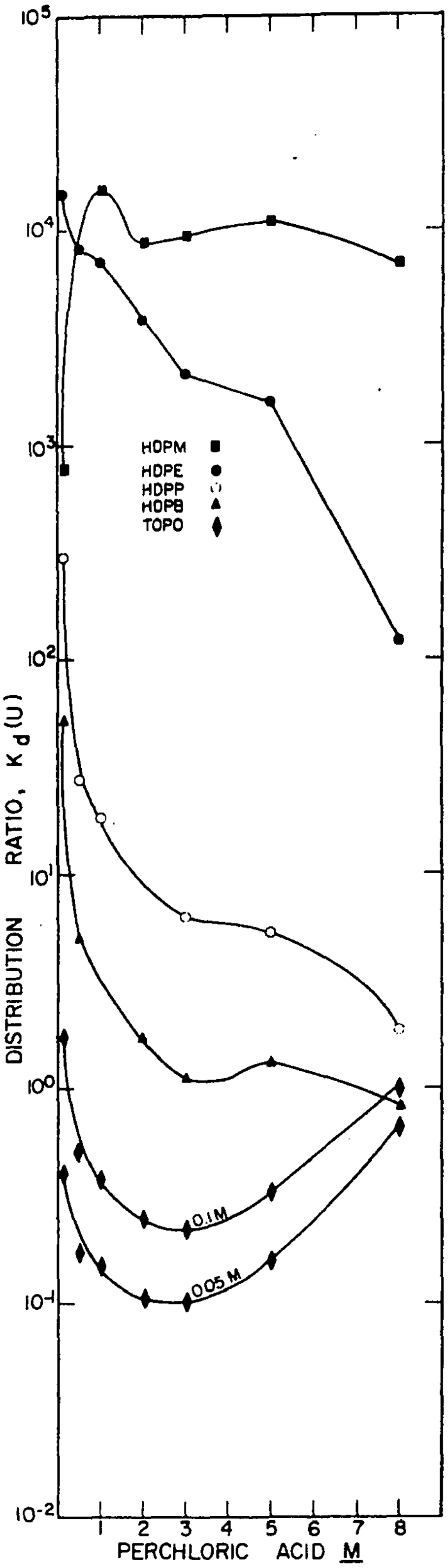

10⁵
10⁴
10³
10²
10¹
10⁰
10⁻¹
10⁻²
DISTRIBUTION RATIO, K_d(U)
1 2 3 4 5 6 7 8
PERCHLORIC ACID M
HDPM ■
HDPE ●
HDPP ○
HDPB ▲
TOPO ♦
0.1M
0.05 M

Table 11. Solvent extraction of uranium(VI) perchlorate with HDPM, HDPE, HDPP, HDPB and TOPO

	Distribution ratio, $K_d(U)$					
$HClO_4$, M	HDPM	HDPE	HDPP	HDPB	TOPO	
						a
0.1	786	15,000	299.7	51.1	0.414	1.75
0.5	8,100	8,200	27.4	4.95	0.184	0.507
1	15,000	7,000	18.1	3.21	0.148	0.384
2	8,600	3,800	9.12	1.72	0.106	0.248
3	9,300	2,100	6.29	1.10	0.102	0.216
5	10,900	1,600	5.34	1.31	0.160	0.329
8	6,800	120.9	1.85	0.826	0.673	1.02

Conditions: organophosphorus compound-0.05 M (unless otherwise indicated)
uranium(VI) perchlorate---0.01667 M
1:1 phase ratio
diluent-1,2-dichlorobenzene

a TOPO-0.1 M

Table 12. Extraction of uranium(VI) perchlorate with HDPM and HDPE using 3:1 and 2:1 ligand/metal ratios

	Distribution ratio, $K_d(U)$	
	3:1, L/M	2:1, L/M
HDPM	786	3.40
HDPE	15,000	6.55

Conditions:

3:1 L/M--$HClO_4$ = 0.1 M; ligand = 0.05 M; U = 0.01667 M

2:1 L/M--$HClO_4$ = 0.1 M; ligand = 0.05 M; U = 0.025 M

1:1 phase ratio

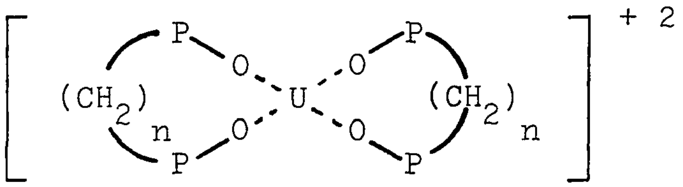
diluent-1,2-dichlorobenzene

Table 13. Loading capacity of HDPM, HDPE, HDPP and HDPE with 1 M uranium(VI) perchlorate

Compound	Concentration, M	Ratio, HDPX/U
HDPM	1.004×10^{-2}	2.1
HDPE	1.000×10^{-2}	2.0
HDPP	7.50×10^{-3}	2.1
HDPB	7.50×10^{-3}	2.0
	diluent-1,2-dichlorobenzene	

perchlorate (pH = 2).

The formation and complete extraction of a disolvated uranium(VI) perchlorate complex with HDPM and HDPE would seem to require the coordination of four phosphoryl oxygens because of the non-coordinating tendencies of the perchlorate ion. This would require six- and seven-membered ring formation,



n = 1,2 ,

where the coordinating ligands are in the plane of the paper and the two uranyl oxygens (not shown) are above and below this plane.

The nature of the complexes formed with HDPP and HDPB can not be adequately explained. Competition for available ligand sites by the proton should be more important for these two compounds (Figure 4) but it would also seem possible that four phosphoryl groups are not able to coordinate to the uranium atom because of the length of the bridging chain. Both effects are expected to be more important for HDPB than for HDPP and seemingly are reflected in the data.

TBP has been found to extract uranium(VI) perchlorate quite well from higher concentrations of perchloric acid (43). Since TBP is a monodentate ligand, theoretically a greater number of TBP molecules should be required to effectively solvate the uranyl ion in perchlorate media. Naito and Suzuki (74) have recently reported that a tetrasolvated complex was formed with TBP and uranium(VI) perchlorate. These findings would seem to support the postulated complex structure for HDPM and HDPE.

In order to complete the picture, the rather poor extraction of uranium perchlorate by TOPO must be explained. Molecular models of TBP and TOPO show that the alkoxy groups around TBP provide reduced steric "crowding" around the phosphoryl oxygen as compared to the alkyl groups around TOPO. The oxygen of the P-O-R linkage permits the phosphoryl oxygen to project out away from the remainder of the molecule thus presumably allowing four molecules of TBP to coordinate to uranium in the presence of the non-coordinating perchlorate anion. TOPO, because of steric crowding by the adjacent methylene groups, is unable to coordinate four molecules to uranium and thus forms a less extractable complex.

The steady decrease in extraction with increasing acid for HDPE was probably due to the competing effect of acid complexation whereas HDPM was only slightly affected by this effect (Figure 7). This agreed qualitatively with the comparative acid extraction data (Table 5, Figure 4).

The slight increase in $K_d(U)$ for TOPO at higher acid concentrations could be due to decreasing water activity. Since extraction was very low over the complete range of acid concentrations, proton competition was certainly not the determining factor in the extraction of uranium(VI) perchlorate. However, decreased water activity would tend to salt out the metal ion to some extent and thus lead to increased distribution ratios.

Partition of Some Lanthanides with HDPM, HDPE, HDPP and HDPB

Partition data for the solvent extraction of praseodymium, neodymium, samarium and thulium by HDPM, HDPE, HDPP and HDPB were studied to evaluate these reagents as a possible means of separating the lanthanide elements. Distribution data were obtained for extractions from aqueous nitric, hydrochloric and perchloric acids to determine the effect of each of these anions on the solvent extraction behavior of the lanthanides.

The distribution ratios from hydrochloric acid were very low for all four lanthanides and thus are presented only in tabular form (Table 14).

Comparisons of the extraction of Nd from nitric and perchloric acids by HDPM, HDPE, HDPP and HDPB are presented in Figures 8-13. The dashed arrows following the last experimental point indicate that the amount of metal extracted for all succeeding acid concentrations was below the sensitivity of the analytical method (titrimetric) used in these investigations. Data comparing the extraction of neodymium from nitric and perchloric acids (Figure 8, 11) with HDPM, HDPE, HDPP and HDPB are typical of the data for praseodymium, samarium and thulium and thus only data from one lanthanide element are presented in figure form. Data for the remaining elements are reported in Table 14.

Extraction from nitric acid

Generally, the data indicated very similar extraction from nitric acid for all four compounds with the largest distribution ratios occuring at 1 M acid concentration. HDPB generally had the largest distribution ratio for extractions from 0.1 M acid whereas HDPE had the largest distribution ratio for all higher acid concentrations. HDPM was the poorest extractant at 0.1 M nitric acid but was second only to HDPE at all higher acid concentrations.

Figure 8. Variations in the distribution ratio of neodymium nitrate with increasing acid concentration at constant ligand concentration (0.05$\underline{M}$) and constant ligand/M (3:1)

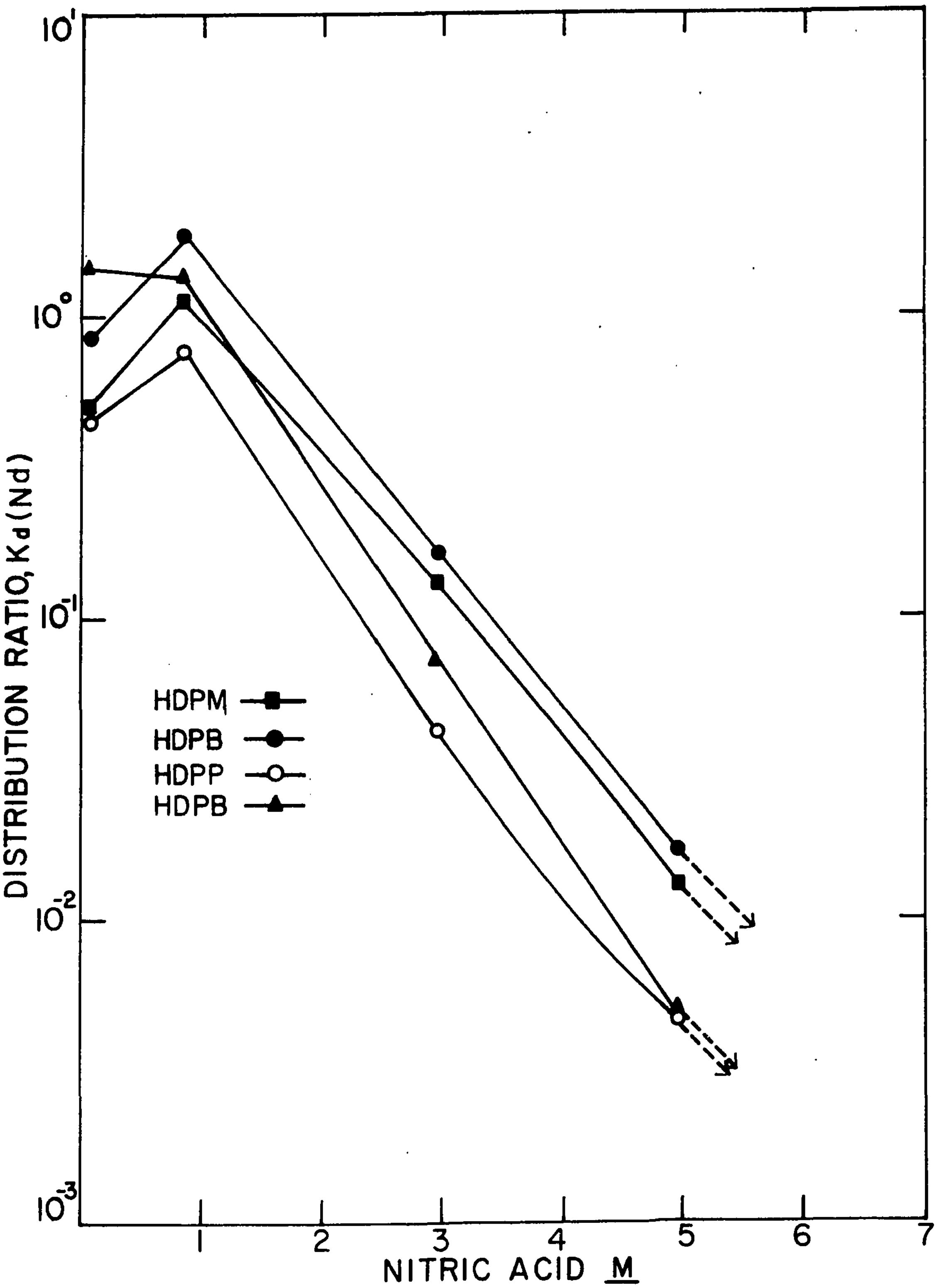

10^1
10^0
10^{-1}
10^{-2}
10^{-3}
DISTRIBUTION RATIO, Kd (Nd)
1
2
3
4
5
6
7
NITRIC ACID M
HDPM ■
HDPB ●
HDPP ○
HDPB ▲

Figure 9. Variation in lanthanide distribution ratios with increasing acid concentration at constant HDPM concentration (0.05M) and constant HDPM/M (3:1)

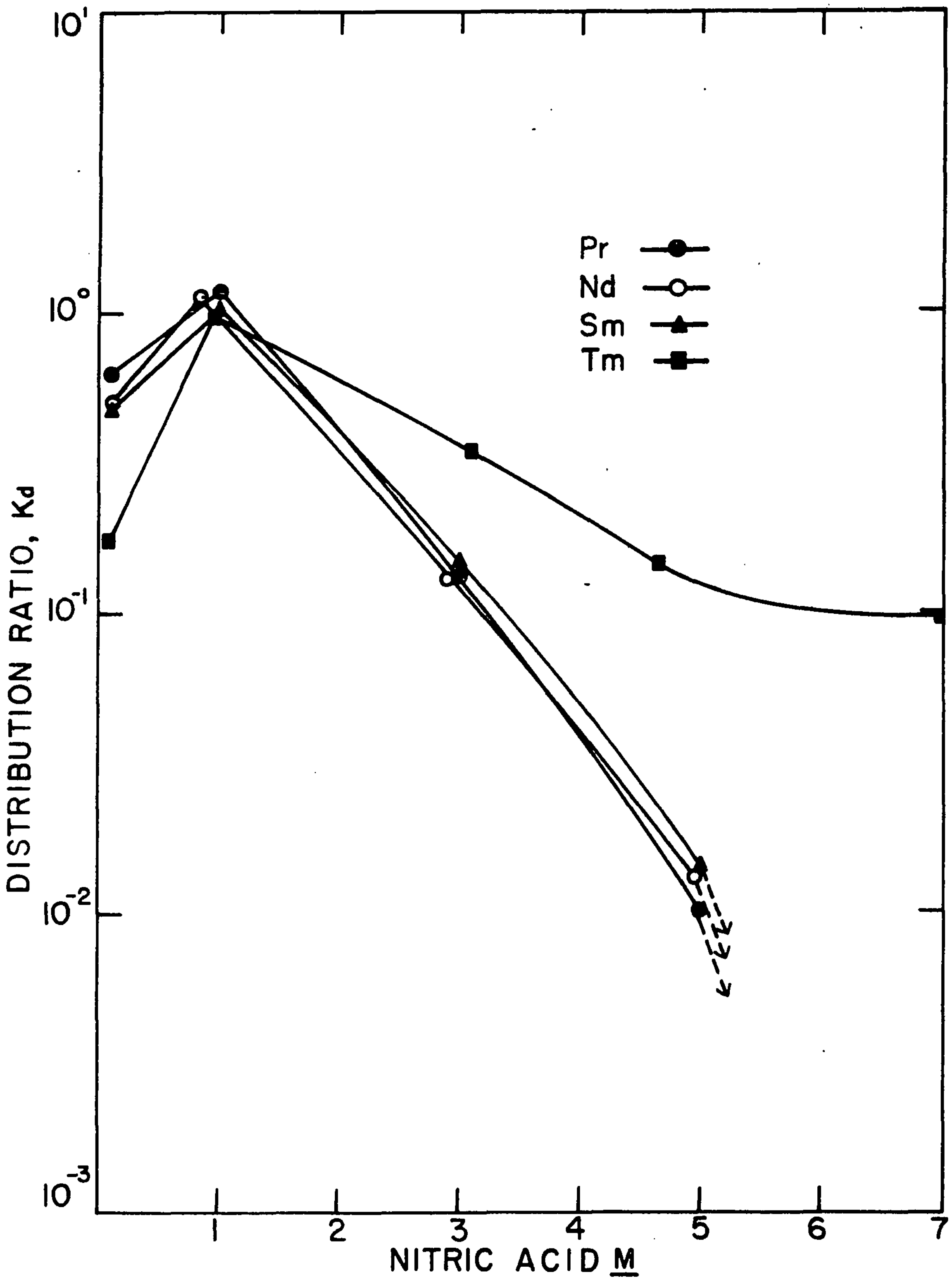

Pr ●
Nd ○
Sm ▲
Tm ■
10^1
10^0
10^{-1}
10^{-2}
10^{-3}
DISTRIBUTION RATIO, Kd
1
2
3
4
5
6
7
NITRIC ACID M

Figure 10. Variation in lanthanide distribution ratios with increasing acid concentration at constant HDPE concentration (0.05M) and constant HDPE/M (3:1)

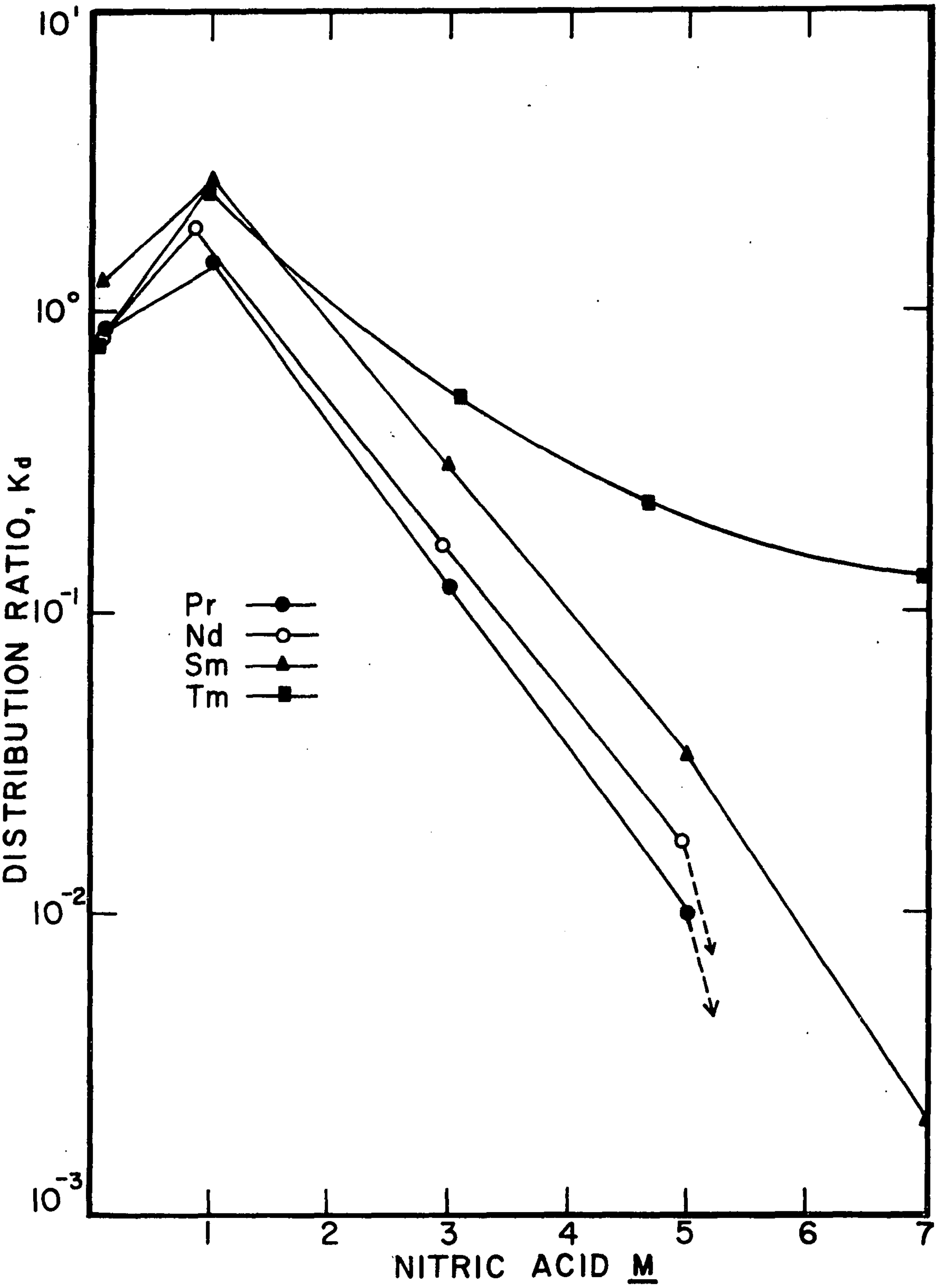

10¹
10⁰
10⁻¹
10⁻²
10⁻³
DISTRIBUTION RATIO, Kd
1
2
3
4
5
6
7
NITRIC ACID M
Pr
Nd
Sm
Tm

Figure 11. Variations in the distribution ratio of neodymium perchlorate with increasing acid concentration at constant ligand concentration (0.05<u>M</u>) and constant ligand/M (3:1)

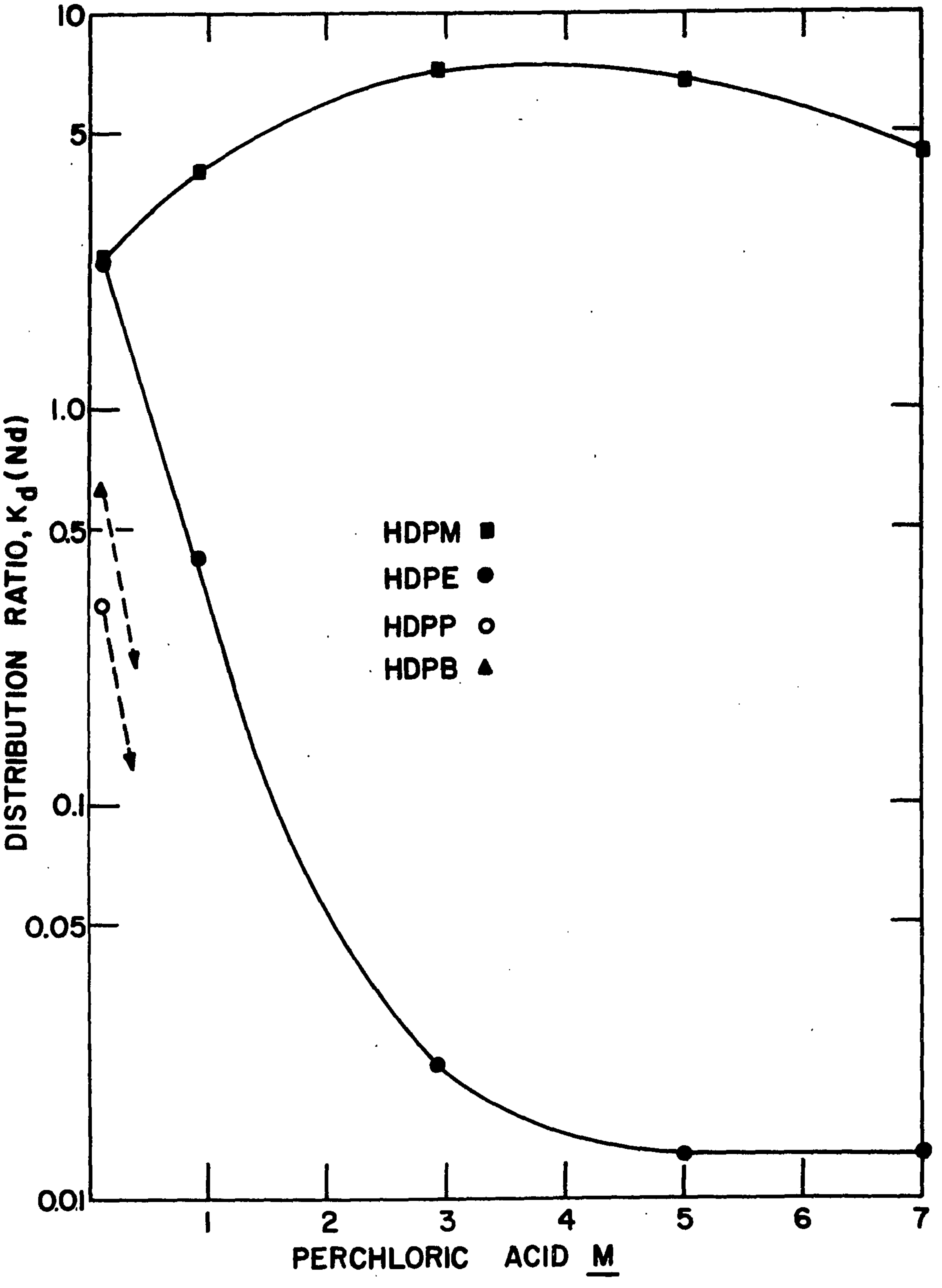

10
5
1.0
0.5
0.1
0.05
0.01
DISTRIBUTION RATIO, K_d (Nd)
1
2
3
4
5
6
7
PERCHLORIC ACID M
HDPM ■
HDPE ●
HDPP ○
HDPB ▲

Table 14. Lanthanide partition data; hydrochloric, nitric and perchloric acid media with HDPM, HDPE, HDPP and HDPB

		Distribution ratio			
Element	Acid, $\underline{M}$	HDPM	HDPE	HDPP	HDPB
Pr	HCl, 0.1	<0.001	<0.001	<0.001	<0.001
	0.6	<0.001	<0.001	<0.001	<0.001
	2	0.008	0.002	<0.001	<0.001
	4	0.006	0.002	<0.001	<0.001
	6	0.073	0.018	<0.001	<0.001
	HNO_3, 0.1	<0.001	0.261	0.459	1.32
	1	1.45	1.42	0.604	1.02
	3	0.13	0.12	0.035	0.053
	5	0.018	0.011	<0.001	<0.001
	7	0.008	<0.001	<0.001	<0.001
	$HClO_4$, 0.1	2.66	2.93	0.226	0.605
	1	3.75	0.470	<0.001	<0.001
	3	5.84	0.039	<0.001	<0.001
	5	5.75	0.026	<0.001	<0.001
	7	4.10	0.023	<0.001	<0.001
Nd	HCl, 0.1	<0.001	<0.001	<0.001	<0.001
	1	<0.001	<0.001	<0.001	<0.001
	3	<0.001	<0.001	<0.001	<0.001
	5	0.017	0.002	<0.001	<0.001
	7	0.097	0.003	<0.001	<0.001
	HNO_3, 0.1	0.501	0.842	0.461	1.42
	1	1.13	1.88	0.768	1.36
	3	0.130	0.162	0.042	0.072
	5	0.013	0.017	0.005	0.005
	7	<0.001	<0.001	<0.001	<0.001
	$HClO_4$, 0.1	2.39	2.42	0.320	0.627
	1	3.99	0.422	<0.001	<0.001
	3	7.13	0.022	<0.001	<0.001
	5	6.68	0.013	<0.001	<0.001
	7	4.43	0.013	<0.001	<0.001

Table 14. (Continued)

		Distribution ratio			
Element	Acid, M	HDPM	HDPE	HDPP	HDPB
Sm	HCl, 0.1	<0.001	<0.001	<0.001	<0.001
	1	<0.001	<0.001	<0.001	<0.001
	3	<0.001	<0.001	<0.001	<0.001
	5	0.034	0.003	<0.001	<0.001
	7	0.201	0.010	<0.001	<0.001
	HNO_3, 0.1	0.481	1.25	0.777	2.24
	1	1.02	2.75	1.06	1.73
	3	0.144	0.306	0.077	0.130
	5	0.014	0.038	0.008	0.003
	7	<0.001	0.002	0.003	<0.001
	$HClO_4$, 0.1	3.03	3.72	0.275	0.616
	1	5.47	0.679	<0.001	<0.001
	3	10.1	0.036	<0.001	<0.001
	5	8.72	0.023	<0.001	<0.001
	7	6.24	0.001	<0.001	<0.001
Tm	HCl, 0.1	<0.001	<0.001	<0.001	<0.001
	1	<0.001	<0.001	<0.001	<0.001
	3	<0.001	0.002	<0.001	<0.001
	5	0.024	0.014	<0.001	<0.001
	7	0.155	0.061	<0.001	<0.001
	HNO_3, 0.1	0.171	0.796	0.396	1.77
	1	0.982	2.59	0.754	2.23
	3	0.344	0.509	0.107	0.303
	5	0.147	0.230	0.040	0.150
	7	0.096	0.130	0.019	0.085
	$HClO_4$, 0.1	3.51	2.59	0.110	0.306
	1	5.07	0.551	<0.001	<0.001
	3	7.81	0.053	<0.001	<0.001
	5	6.99	0.038	<0.001	<0.001
	7	3.12	0.028	<0.001	<0.001

Comparative partition data for the four lanthanides with HDPM and HDPE are presented in Figures 9 and 10. The data indicate very similar extraction behavior for both of these organophosphorus compounds. The only analytically feasible separation appeared to be Tm from the other three lanthanides using an aqueous phase consisting of 7 M nitric acid. Separation factors were of the order 10-20 for HDPM and HDPE using that concentration of acid. There appeared to be no possibility of separating Pr, Nd and Sm from each other by a single extraction under the conditions explored in this section.

Extraction from perchloric acid

Very distinct differences in distribution ratios were observed for Nd when comparing the four solvent extractants (Figure 11). The extraction by HDPM was considerably better than the other three reagents for acid concentrations in excess of 0.1 M. This trend was very similar to that found for uranium(VI) perchlorate (Figure 7). HDPE exhibited an initial rapid decrease in extraction followed by a leveling off at 5 M acid concentration. HDPP and HDPB extracted negligible amounts of the lanthanides for all perchloric acid concentrations in excess of 0.1 M.

Comparing the individual lanthanides using the same extractant, one anomaly was noted in extractions with HDPM (Figure 12). Thulium exhibited the opposite reversal that was noted for extractions from nitric acid (Figure 9). (Reversal refers to the fact that, on one end of the acidity scale the distribution ratio for a particular lanthanide was the largest (smallest) of the four while on the opposite end of the acidity scale the distribution ratio was the smallest (largest) of the four elements.) In perchloric acid the highest distribution ratio was observed for extractions from 0.1 M acid while the lowest was observed for 7 M acid concentration. Thulium maintained the same position relative to the other lanthanide elements as was observed in nitric acid for extractions with HDPE (compare Figure 10 and 13). Very little difference in distribution ratio was noted for extractions from perchloric acid and thus no analytically useful separation factor was obtained.

Synergism

The word synergism, as used in solvent extraction systems, is defined as the cooperative action of discrete reagents such that the total effect is larger, when these reagents are used in combination, than the sum of the effects obtained when they are used independantly.

Blake and others (13) first reported synergistic enhancement of distribution ratios in organophosphorus solvent extraction systems composed of dialkylphosphoric acids and neutral organophosphorus compounds. They reported that synergistic enhancement seemed to be limited to dialkylphosphoric acid-neutral reagent combinations and, referring to the elements V, Th, Al, rare earths, Fe and U which they had studied, uranium

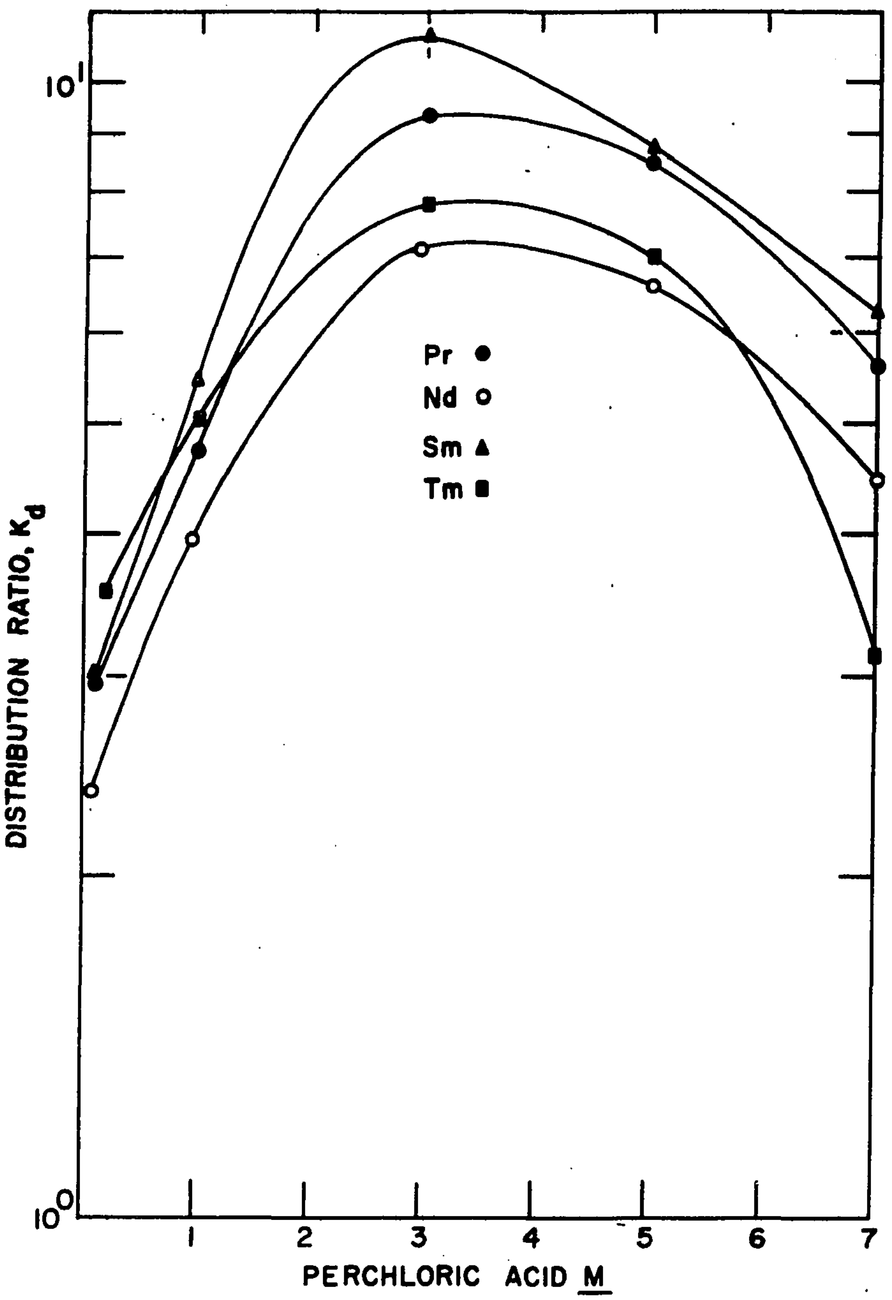
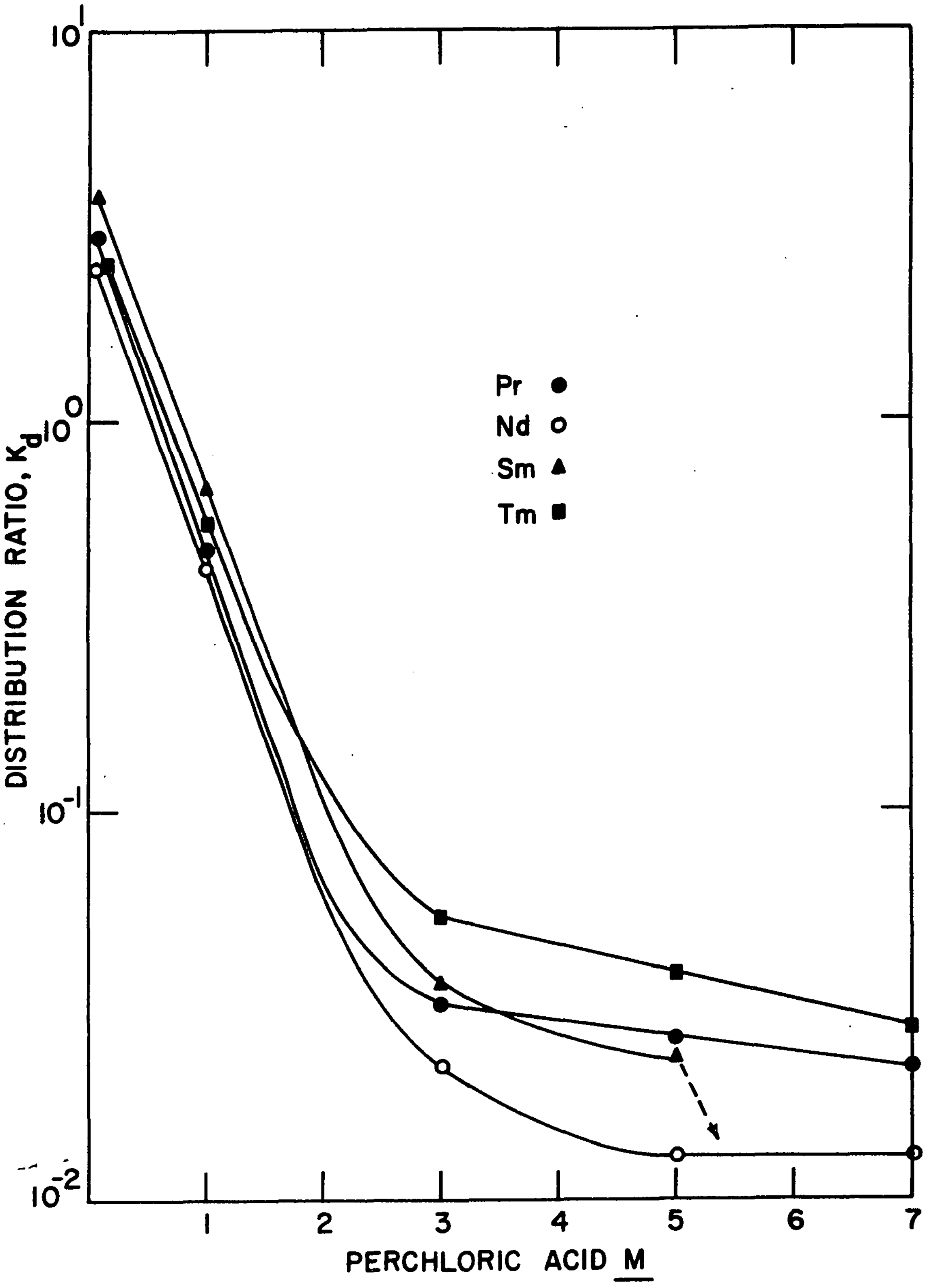


Figure 12. Variation in lanthanide distribution ratios with increasing acid concentration at constant HDPM (0.05M) concentration and constant HDPM/M (3:1)

Figure 13. Variation in lanthanide distribution ratios with increasing acid concentration at constant HDPE concentration (0.05$\underline{M}$) and constant HDPE/M (3:1)


10^1
10^0
10^{-1}
10^{-2}
DISTRIBUTION RATIO, K_d
Pr ●
Nd ○
Sm ▲
Tm ■
1
2
3
4
5
6
7
PERCHLORIC ACID M

was the only metal that was extracted synergistically. Irving and Edgington (48) disagreed with these findings; they regarded these phenomena as being more widespread and not limited to just uranium. Their considerations of the problem of synergic enhancement led them to expect this to occur in a number of solvent extraction systems provided that four sufficient conditions were fulfilled:

(i) One of the active solvents should be capable of neutralizing the charge on the metal ion, preferably by forming a chelated complex.
(ii) The second active solvent must be capable of displacing any residual coordinated water from the formally neutral metal complex and rendering it less hydrophilic.
(iii) The second active solvent is not in itself hydrophilic and is coordinated less strongly than the first (chelating) solvent.
(iv) The maximum coordination number of the metal and the geometry of the ligands must be favorable.

These conditions have proved reliable in choosing solvent extraction systems which can be expected to provide synergistic enhancement phenomena.

Synergistic enhancement of partition was investigated briefly for the systems praseodymium-thenoyltrifluoroacetone (TTA)-HDPM (or HDPE) from nitric and perchloric acid media. A strong enhancement effect was noted for both HDPM and HDPE with this lanthanide element (Table 15). The enhancement seemed to be much greater in the presence of the non-coordinating anion, perchlorate than in the presence of nitrate. The hydrogen ion concentration appeared to affect the extraction

Table 15. Synergism studies of TTA-HDPM (HDPE) systems with praseodymium

Acid, M	Extractant, M	Distribution ratio
$HClO_4$, 7 x 10^{-4}	HDPM, 0.05	1.82
	HDPE, 0.05	2.12
	TTA, 0.10	<0.001
	TTA-HDPM, 0.01-0.05	4.18
	TTA-HDPM, 0.10-0.05	120
	TTA-HDPE, 0.10-0.05	605
$HClO_4$, 1 x 10^{-2}	HDPM, 0.05	2.02
	HDPE, 0.05	2.68
	TTA, 0.10	<0.001
	TTA-HDPM, 0.01-0.05	4.68
	TTA-HDPM, 0.10-0.05	121
	TTA-HDPE, 0.10-0.05	303
HNO_3, 6 x 10^{-3}	HDPM, 0.05	0.094
	HDPE, 0.05	0.212
	TTA, 0.10	0.001
	TTA-HDPM, 0.01-0.05	0.353
	TTA-HDPM, 0.10-0.05	3.00
	TTA-HDPE, 0.10-0.05	6.40
HNO_3, 1 x 10^{-1}	HDPM, 0.05	0.608
	HDPE, 0.05	0.850
	TTA, 0.10	0.001
	TTA-HDPM, 0.01-0.05	0.588
	TTA-HDPE, 0.10-0.05	2.66

Conditions: Pr-0.01667 M
1:1 phase ratio
diluent-1,2-dichlorobenzene

of the HDPE-TTA system more than that of HDPM-TTA. This of course was similar to results obtained using these organophosphorus compounds alone as solvent extractants.

Cuninghame and others (23) reported solvent extraction studies of praseodymium and neodymium using TTA-TBP mixtures. They observed a large enhancement of distribution ratios for both elements. Their findings showed separation factors of the order of two to three and they concluded that this system provided no improvement in separation factors for adjacent lanthanides over those obtained with TBP alone.

Complexes of Uranium(VI) Nitrate with HDPM, HDPE, HDPP, HDPB and TOPO

Determination of the solvation number by "slope" method

It is customary to identify the slope of a logarithmic plot of distribution coefficient versus solvent concentration with the solvation number of the extracted complex. This can best be shown by means of the following reaction and example,

$$M^{+n}_{(a)} + nX^{-1}_{(a)} + \nu S_{(o)} \longrightarrow MX_n \cdot \nu S_{(o)} \quad ,$$

where (a) and (o) refer to aqueous and organic phases, respectively. At equilibrium, the overall formation constant is given by Equation 2.

$$K = \frac{\left[MX_n \cdot \nu S\right] \gamma_c}{\left[M^{+n}\right] \left[X^{-1}\right]^n \gamma_{\pm}^{n+1} \left[S\right]^{\nu} \gamma_s^{\nu}} \qquad (2)$$

The symbols γ_c, γ_s, and $\gamma_{\pm}$ are the activity coefficients of the extracted complex, the extractant, and the mean activity coefficient of the metal salt in the aqueous phase. Assuming that dilute solutions are used and the aqueous phase is held at constant ionic strength, Equation 2 can be rearranged as shown in Equation 3

$$K \frac{\gamma_s^{\nu} \gamma_{\pm}^{n+1}}{\gamma_c} = K' = \frac{C_m - [M]_{(a)}}{[M^{+n}]_{(a)} [X^{-1}]^n_{(a)} [S]^{\nu}_{(a)}} \qquad (3)$$

where C_m = initial metal concentration and

$[M]_{(a)}$ = total metal concentration remaining in aqueous phase. Equation 3 can be simplified as shown in Equation 4.

$$K' = \frac{K_d(M)}{[X^{-1}]^n_{(a)} [S]^{\nu}_{(o)}} \qquad (4)$$

or

$$\log K'' = \log K_d(M) - \nu \log [S]_{(o)}$$

since $K' [X^{-1}]^n_{(a)} \approx$ constant, when trace metal concentration and a sufficiently high, constant ionic strength are employed. The quantity, $[S]_{(o)}$ is approximately equal to the initial concentration of solvent if present in great excess therefore a logarithmic plot of $K_d(M)$ versus solvent concentration will be a straight line of slope ν which is the solvation number. The previous derivation is only valid in concentration ranges where ideal behavior is followed, e.g., in dilute solutions of both metal and solvent (44).

Logarithmic plots of distribution ratio versus solvent concentration for the extraction of uranium(VI) nitrate by HDPM, HDPE, HDPP, HDPB and TOPO are depicted in Figures 14 and 15. Both sets of data represent extractions from aqueous phases containing the same total nitrate concentration (0.0126 M) and uranium(VI) concentration (5×10^{-5} M) but differing in their hydrogen ion concentrations. The data for Figure 14 represent extractions from an aqueous phase containing 2.48×10^{-3} M nitric acid with the total nitrate concentration adjusted to 0.0126 M with potassium nitrate while the data for Figure 15 are for an aqueous phase containing 0.0125 M nitric acid and the same total nitrate (0.0126 M).

The lower portions of the curves for HDPM had a slope of two and thus indicated that a disolvated complex $[UO_2(NO_3)_2 \cdot 2HDPM]$ was formed. As the ligand/metal ratio increased byond 200:1, the slope increased from 2 to 2.65 (Figure 14) and from 2 to 2.45 (Figure 15). These data may be indicative of the formation of a trisolvate $[UO_2(NO_3)_2 \cdot 3HDPM]$ or some other higher complex. The stability of this complex relative to the disolvated complex appeared to be rather low since the slope did not rise above two until the ligand/metal

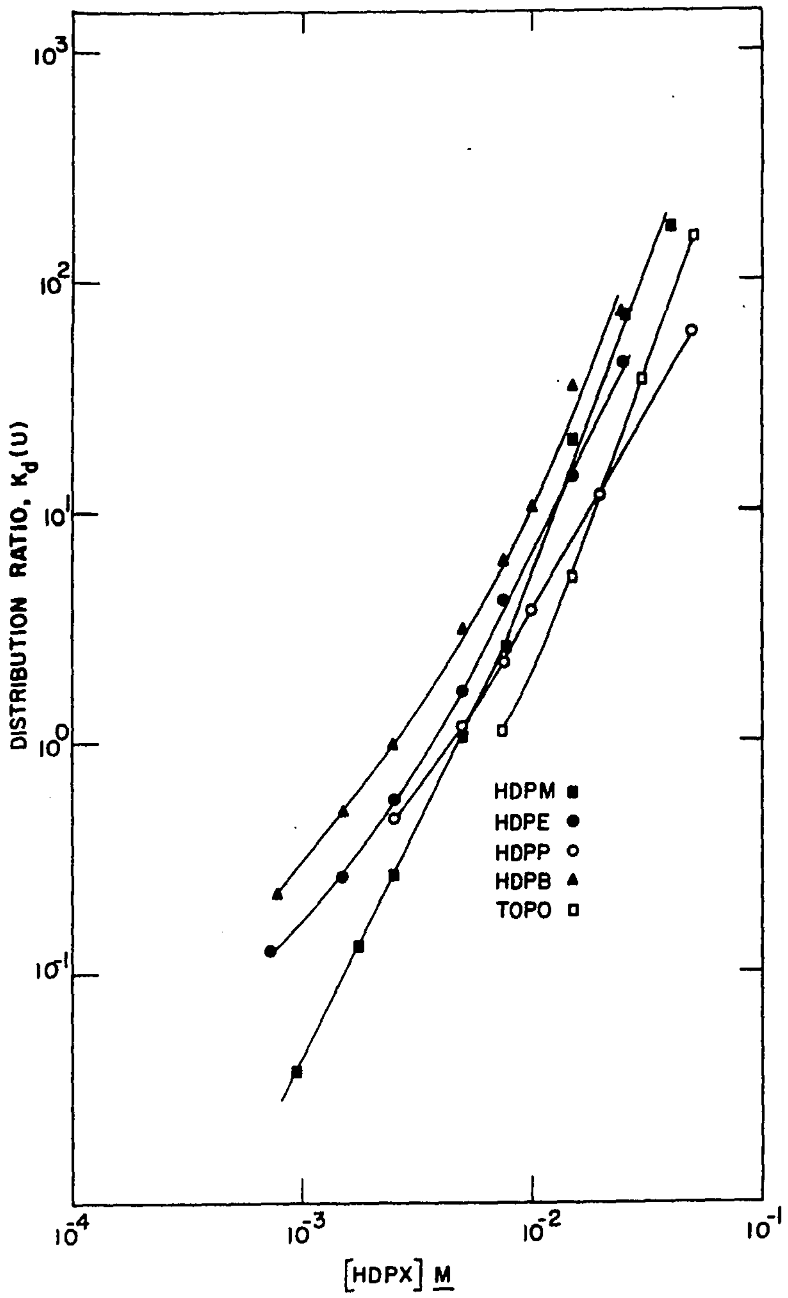


Figure 14. Variations in the distribution ratio of uranium(VI) nitrate with increasing solvent concentrations; $U_1 = 5\text{x}10^{-5}\underline{M}$, $H^{+1} = 2.5\text{x}10^{-3}\underline{M}$, $NO_3^{-1} = 1.26\text{x}10^{-2}\underline{M}$; slopes---HDPM-2→2.65, HDPE-2, HDPP-1.6, HDPB-1.3→2.3, TOPO-2.8

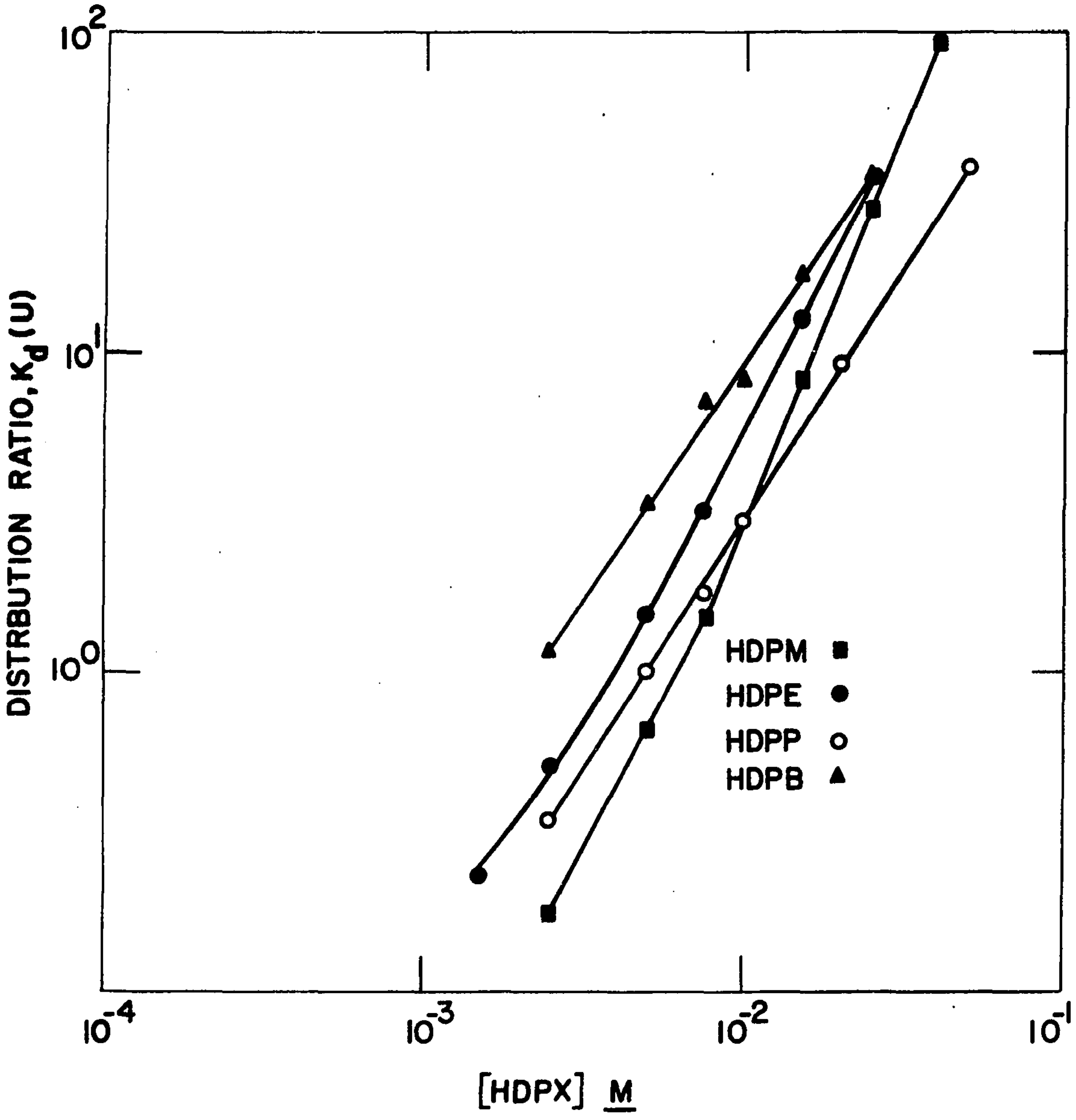


Figure 15. Variations in the distribution ratio of uranium (VI) nitrate with increasing solvent concentrations; $U = 5x10^{-5}\underline{M}$, $H^{+1} = 1.25x10^{-2}\underline{M}$, $NO_3^{-1} = 1.26x10^{-2}\underline{M}$; slopes---HDPM-2→2.45, HDPE-1.9, HDPP-1.6, HDPB-1.5

ratio was greater than 200.

Slopes of two were obtained for HDPE (Figure 14, 15) and indicated disolvate formation $\left[UO_2(NO_3)_2 \cdot 2HDPE\right]$. No evidence for the formation of a higher complex was observed.

The slope data for HDPP and HDPB were rather inconclusive. The data did indicate that if a disolvate was formed with either of these compounds, it was not very stable. The slope of 1.5 obtained for HDPB (Figure 15) at higher acid concentration was changed considerably upon decreasing the acid concentration (Figure 14). The slope of 1.5 may indicate a 3:2 complex $\left[2UO_2(NO_3)_2 \cdot 3HDPB\right]$ although this requires further verification. The slope obtained at low acid concentration was constantly changing and ranged from 1.3 to 2.3 as extremes. The slopes obtained for HDPP were approximately the same for both acid concentrations (1.65-Figure 14; 1.57-Figure 15) and no conclusions may be drawn about the solvation number.

A slope of 2.8 was obtained for TOPO (Figure 14), this was regarded as supporting evidence for the formation of a trisolvated complex $\left[UO_2(NO_3)_2 \cdot 3TOPO\right]$. The fact that the slope never reached three, even in the presence of a great excess of ligand, indicated that this complex was not the principal species in solution. White and Ross (114) reported that the disolvated complex was the extracted species in the solvent extraction of uranium(VI) nitrate.

Calculation of equilibrium constants

Equilibrium constants were calculated for the disolvated complexes of HDPM and HDPE. Calculations were made according to Equation 3 utilizing data from Figures 14 and 15 where the slope was two (Table 16). A slight reduction in the formation constants was noted for extraction data from the higher acid concentration. This probably was caused by a slight decrease in uncomplexed ligand due to acid complexation.

It was found that the conditional constant for extractions of uranium(VI) nitrate from 1 M nitric acid with moderate excesses of HDPM could be related to the constant obtained for extractions from very low concentrations of nitric acid by calculating the complexation effect of the nitric acid (71). The following overall reaction describes the extraction of uranium (VI) from aqueous nitrate media using moderate excesses of the extractant.

$$UO_{2(a)}^{+2} + 2\ NO_{3(a)}^{-1} + 2\ HDPM_{(o)} \longrightarrow UO_2(NO_3)_2 \cdot 2HDPM_{(o)}$$

The expression for the overall equilibrium constant is given by Equation 5.

$$K_2 = \frac{\left[UO_2(NO_3)_2 \cdot 2HDPM\right] \gamma_c}{\left[UO_2^{+2}\right]\left[NO_3^{-1}\right]^2 \gamma_\pm^3 \left[HDPM\right]^2 \gamma_S^2} \qquad (5)$$

Table 16. Equilibrium constants, K'_2, for the disolvated uranium(VI) nitrate complexes of HDPM and HDPE

		a			b	
	$[HDPX]^*_o$ ($\times 10^3$)	$K_d(U)$	K'_2 ($\times 10^{-8}$)	$[HDPX]^*_o$ ($\times 10^3$)	$K_d(U)$	K'_2 ($\times 10^{-8}$)
HDPM	7.656	2.634	2.93	25.01	28.14	2.90
	7.656	2.681	2.98	15.13	8.09	2.29
	5.073	1.011	2.52	7.656	1.48	1.62
	2.501	0.264	2.70	5.073	0.662	1.65
	1.76	0.120	2.46	2.501	0.174	1.78
	0.9503	0.0316	2.22		Average	2.05
		Average	2.64			
HDPE	25.0	44.01	4.54	25.0	34.84	3.59
	15.0	15.26	4.39	15.0	12.7	3.65
	15.0	13.08	3.76	7.50	3.19	3.64
	7.50	4.06	4.65	4.997	1.52	3.92
	4.997	1.65	4.28		Average	3.70
		Average	4.32			

$[\;]^*$ Initial molar concentrations

Conditions: a $[U]^* = 5.07 \times 10^{-5}$ M; $[H^+]^* = 2.48 \times 10^{-3}$ M;
$[NO_3^-]^* = 1.26 \times 10^{-2}$ M

b $[U]^* = 5.07 \times 10^{-5}$ M; $[H^+]^* = 1.25 \times 10^{-2}$ M;
$[NO_3^-]^* = 1.26 \times 10^{-2}$ M

The symbols γ_c, γ_S and $\gamma_{\pm}$ are the activity coefficients of the extracted complex, the extractant and the mean activity coefficient for uranium(VI) nitrate in the aqueous phase. This equilibrium expression (Equation 5) can be rewritten in conditional constant form as shown in Equation 6 and rearranged as shown in Equation 7. Charges have been omitted for clarity.

$$K_2 = \frac{\left[UO_2(NO_3)\cdot 2HDPM\right]\ \gamma_c}{\beta\ \left[UO_2'\right]\left[NO_3\right]^2\ \gamma_\pm^3\ \alpha^2\ \left[HDPM'\right]^2\ \gamma_S^2} \qquad (6)$$

$$UO_2' = UO_2^{+2} + (UO_2NO_3)^{+1} + \text{--------}$$

$$HDPM' = HDPM + HDPM\cdot HNO_3 + \text{--------}$$

The fractions of HDPM as the free extractant and of uranium in the uncomplexed form are represented respectively by α and β.

$$K_2' = \frac{K_2\ \gamma_\pm^3\ \gamma_S^2\ \beta\alpha^2}{\gamma_c} = \frac{K_d(U)}{\left[NO_3\right]^2\ \left[HDPM'\right]^2} \qquad (7)$$

The activity coefficients were assumed to remain relatively constant in dilute solutions and β was approximately one since the formation constant for the nitrate complex of uranium has been reported to be very small (1, 10, 25). Thus, in order to relate the conditional equilibrium constant found for extraction from 1 M nitric acid (Table 17) to the constant found for extraction from low nitric acid concentration (Table 16), α, the fraction of uncomplexed ligand, must be determined as shown in the following expression,

Table 17. Conditional constant, K_2' (1 M) for the extraction of uranium(VI) nitrate with HDPM from 1 M nitric acid

$[HDPM]_o^*$	$[UO_2^{+2}]_a^*$ (x 10^3)	$K_d(U)$	K_2' (1 M) (x 10^{-6})
0.10	25.0	2860	1.14
0.0667	16.7	1060	0.95
0.0445	11.1	414	0.83
0.0320	8.0	213	0.83
0.060	10.0	2350	1.47
0.024	4.0	265	1.03
0.012	2.0	58.8	0.92
0.0024	0.4	3.82	1.22
			Average 1.05

$[\ ]^*$ Initial molar concentrations

$$\alpha^{-1}_{HDPM(H)} = 1 + K_1 \left[H^{+1}\right] \left[NO_3^{-1}\right] \qquad (8)$$

$$\alpha_{HDPM(H)} = 0.062$$

where K_1 is the formation constant for the 1:1 complex of HDPM and nitric acid (Table 7). Taking α as 0.062 and 1 for the cases of extraction from 1 M and 2.48 x 10^{-3} M acid, respectively, one obtains from $\frac{K_2'(1M)}{(0.062)^2}$, a calculated value for K_2' of 2.78 x 10^8. This is in excellent agreement with the experimental value obtained for this constant, 2.64 x 10^8 (Table 16).

Loading capacities have been used extensively to determine the solvation number of the lower complex of a solvent extraction system. Results obtained by this method should be viewed with caution since the organic phase may exhibit different loading values depending upon the media used to effect its saturation and the organic diluent used.

Loading capacities were determined for the organophosphorus compounds used during the course of this investigation. Two diluents, 1,2-dichlorobenzene and 1,2-dichloroethane, were utilized and aqueous 1M uranium(VI) nitrate and the solid, dihydrated salt were used as the saturating media. Table 18 contains the data obtained for both diluents.

Table 18. Saturation of organophosphorus compounds with 1 M uranium(VI) nitrate and $UO_2(NO_3)_2 \cdot 2H_2O$

	Ratio, S/U		
Compound (0.01 M)	1 M $UO_2(NO_3)_2$[a]	$UO_2(NO_3)_2 \cdot 2H_2O$[a]	$UO_2(NO_3)_2 \cdot 2H_2O$[b]
HDPM	1.00	0.90	0.84
HDPE	1.00	0.87	0.75
HDPP	1.01	0.75	0.68
HDPB	1.00	0.76	0.68
TOPO			1.11

[a] diluent-1,2-dichlorobenzene.

[b] diluent-1,2-dichloroethane.

These studies suggested that, in the presence of excess, aqueous uranium(VI) nitrate, a monosolvated complex was formed with the bidentate organophosphorus compounds. When saturations were conducted with the dihydrated uranium(VI) nitrate, metal in excess of that required for a 1:1 complex was found in the organic phase. This can be explained by solvation of the unsaturated coordination sphere of the uranium atom with a single phosphoryl oxygen. In aqueous solution, however, uranium has all available coordination positions filled with water molecules and thus two phosphoryl oxygens are required to displace water and form a extractable complex.

Assuming 1:1 complex formation in the presence of excess aqueous uranium(VI) nitrate, varying concentrations of bidentate organophosphorus compound were equilibrated with a 0.1 M uranium solution containing only enough acid to prevent hydrolysis. Equilibrium constants were calculated according to Equation 9,

$$UO_{2(a)}^{+2} + 2NO_{3(a)}^{-1} + S_{(o)} \longrightarrow UO_2(NO_3)_2 \cdot S_{(o)}$$

$$K_1 = \frac{\left[UO_2(NO_3)_2 \cdot S\right] \gamma_c}{\gamma_{\pm}^3 \left[UO_2^{+2}\right] \left[NO_3^{-1}\right]^2 \left[S\right] \gamma_S} , \qquad (9)$$

where S = HDPM, HDPE, HDPP or HDPB and γ refers to the various activity coefficients. This expression can be rearranged as shown in Equation 10.

$$K_1' = \frac{K_1 \gamma_{\pm}^3 \gamma_S}{\gamma_c} = \frac{K_d(U)}{\left[NO_3^{-1}\right]^2 \left[S\right]} \qquad (10)$$

The equilibrium concentration of solvent, $[S]$, was calculated according to Equation 11.[1]

$$[S] = [S]^* - \left[UO_2(NO_3)_2 \cdot S\right] = [S]^* - \left[\left[UO_2^{+2}\right]^* - \left[UO_2^{+2}\right]_o\right] \qquad (11)$$

Increased separation between the phosphoryl groups appeared to increase the stability of the monosolvated complexes as indicated by the formation constants obtained for this complex (Table 19).

Infrared investigations of complexing

Infrared spectral data have been used empirically to elucidate the nature of metal-organophosphorus complexes (56, 74, 79, 83). However only Nukada and others (79) and Naito and Suzuki (74) have investigated the effect of varying ligand/metal ratios on the infrared spectra.

---

[1] Square brackets indicate equilibrium molar concentrations and $[\;]^*$ indicates initial molar concentration.

Table 19. K_1' values for $UO_2(NO_3)_2 \cdot S$ (S = HDPM, HDPE, HDPP, HDPB)

Compound	K_1' ($\times 10^{-3}$)	No. of determinations
HDPM	2.0 ± 0.9[a]	6
HDPE	5.9 ± 2.0[a]	12
HDPP	7.1 ± 3.9[a]	18
HDPB	8.8 ± 1.9[a]	11

Conditions: $[UO_2^{+2}]^* = 0.10$ M; $[NO_3^{-1}]^* = 0.2021$ M;

$[H^{+1}]^* = 2.04 \times 10^{-3}$ M

[a] Range.

The purpose of this phase of the investigation was to attempt to correlate the differences in infrared spectra caused by varying ligand/metal ratios with proposed structures for the various complexes. Individual solutions (prepared as described in EXPERIMENTAL) containing a constant amount of organophosphorus compound (0.8 mmole-HDPM, HDPE, HDPP, HDPB and TOPO) and varying amounts of uranium(VI) nitrate dihydrate (0.1 to 1.2 mmoles) were prepared in 1,2-dichloroethane (10 ml total volume). This diluent was chosen because its infrared spectrum is free of strong bands in the spectral regions of interest and its dielectric constant (10.36) is similar to that of 1,2-dichlorobenzene (9.93), the other diluent used in these investigations.

TOPO When uranium(VI) nitrate is solvated by an organophosphorus compound such as TOPO, the band representing the vibrations of the uncomplexed P-O entity (1161 cm^{-1}) is shifted in the direction of lower frequencies thus indicating a decrease in the phosphorus-oxygen bond order (Figure 16). This suggested that coordination had occurred between the metal and the electron-rich phosphoryl oxygen thus decreasing the $p\pi \rightarrow d\pi$ back-bonding between phosphorus and oxygen (22) and resulting in a general weakening of this bond.

Three different complexed phosphoryl bands were observed on varying the TOPO/U ratio. Figure 17 shows the absorbance data for these three bands. The band at 1101 cm^{-1} was clearly shown to represent the disolvated complex, $UO_2(NO_3)_2 \cdot 2TOPO$. It has been quite generally agreed that this is the complex which is extracted (14,114) and thus should be the species present in the greatest concentration. Two bands were observed in spectra of the solutions containing the largest amount of excess ligand (8:1, 4:1 and 2.67:1 TOPO/U). One of these bands was due to the disolvated complex while the other, at 1078 cm^{-1}, appeared to be caused by a higher complex. This was demonstrated by adding solid TOPO to the solution containing a 8:1 TOPO/U ratio. It was observed that the absorbance of the band at

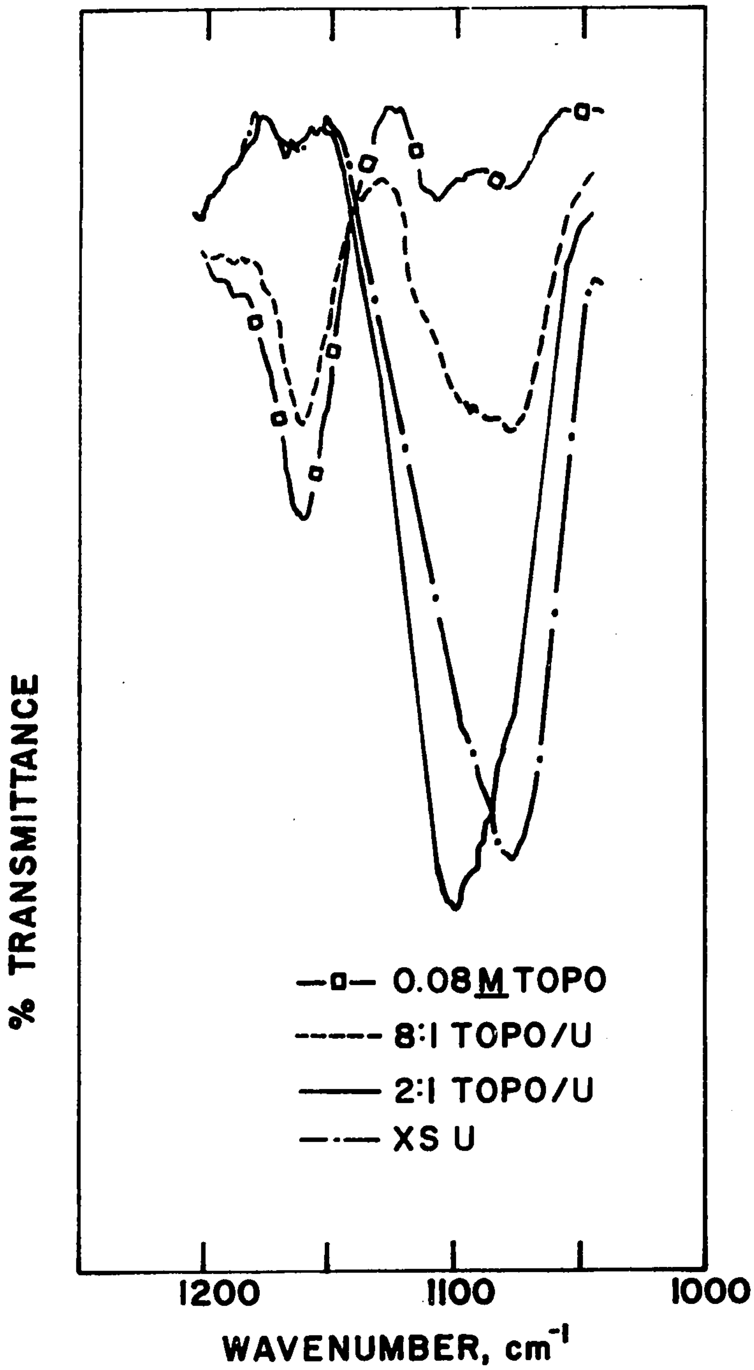


Figure 16. Uncomplexed and complexed phosphoryl spectra of TOPO and $UO_2(NO_3)_2 \cdot \nu TOPO$

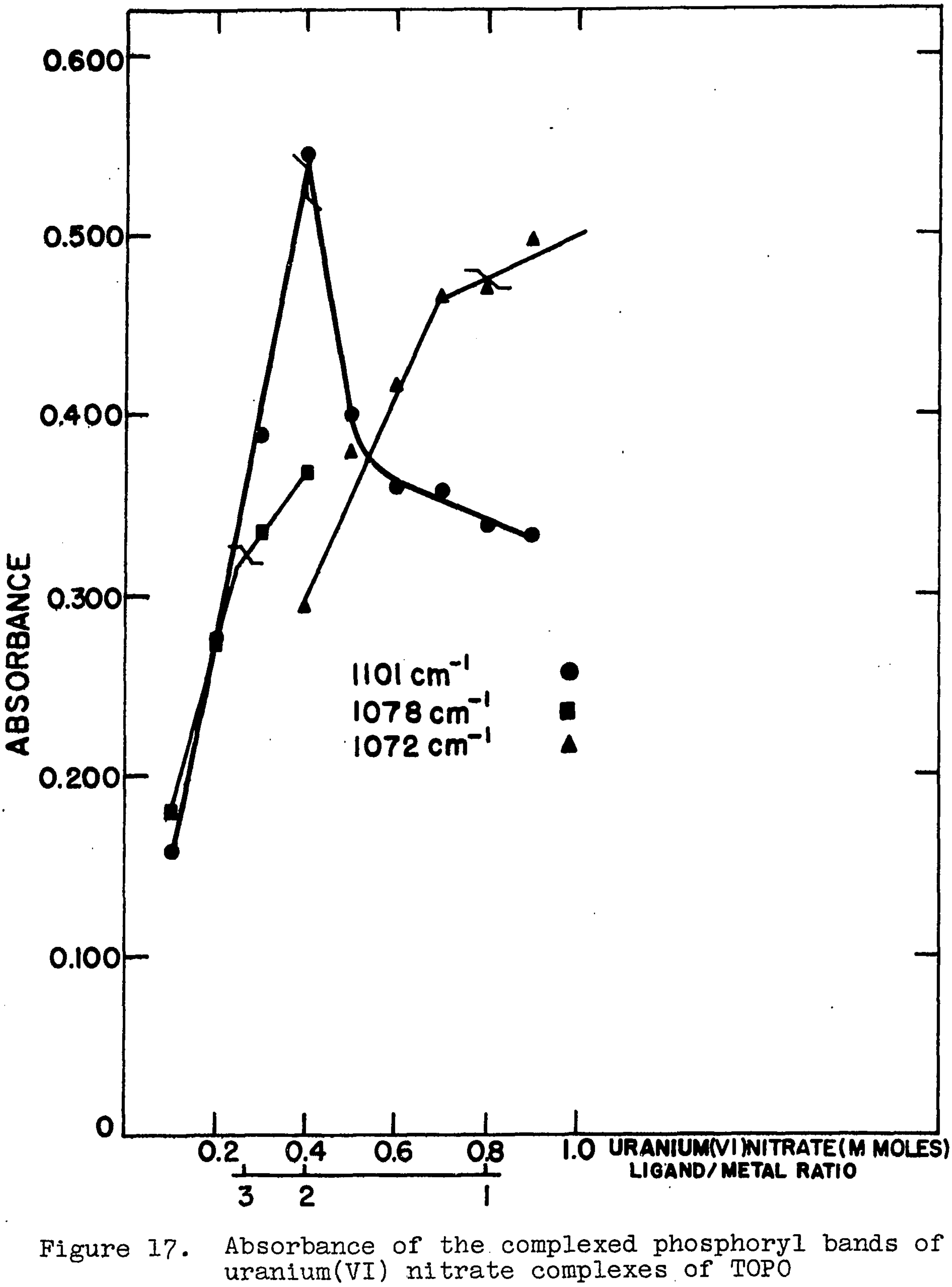


Figure 17. Absorbance of the complexed phosphoryl bands of uranium(VI) nitrate complexes of TOPO

1078 cm^{-1} was increased relative to the band due to the disolvated complex. This would be expected if the band were due to a higher complex since mass action effects should force the reaction in the direction of this complex. The stability of the higher complex relative to the disolvate was thought to be rather low since, even in the presence of eight-fold excess ligand, absorbances of the two bands were approximately equivalent (Figure 16). The absorbance data for this band (Figure 17) appeared to indicate that it was due to a trisolvated complex $\left[UO_2(NO_3)_2 \cdot 3TOPO\right]$ and, since this was in agreement with the partition data (Figure 14), this assignment was assumed correct.

As the TOPO/U ratio was decreased from 2:1 to 1.6:1, the absorbance of the disolvate band at 1101 cm^{-1} decreased considerably and a new band started to grow at 1072 cm^{-1}. The absorbance data for this band (Figure 17) were rather inconclusive but, coupled with the loading capacity of 1.11 TOPO/U (Table 18), it was assumed that the band was caused by a monosolvated complex, $UO_2(NO_3)_2 \cdot TOPO$. Since incomplete formation of this species was indicated by the loading capacity, the mole-ratio break could not be expected to occur at a 1:1 ratio.

Jones (53) reported that the observation of two vibrational frequencies, ν_3 (asymmetric stretching) and $\nu_1+\nu_3$ (combination band; ν_1 is the symmetric stretching frequency) of the uranyl group, served as a very sensitive measure of the

U-O bond distance. It was impossible to assign the combination band $\nu_3+\nu_1$, but Table 20 contains the frequency data for the ν_3 band. These data indicate that negligible changes in the U-O bond order have occured. This would seem to indicate that another donor group has replaced the phosphoryl oxygen as the complex changes from a disolvate to monosolvate on decreasing the TOPO/U ratio below 2:1. This other donor group could be one or more water molecules; this would maintain the electron density at approximately the same magnitude and allow the ν_3 band to remain invariant.

The frequency shifts observed for the different complexes of TOPO and uranium illustrate the danger of attempting to relate increased complex stability with increased separation between complexed and uncomplexed phosphoryl bands (73, 84). The frequency shift observed for the disolvate, presumably the most stable complex, was 60 cm^{-1} while those of the monosolvate and trisolvate were 89 cm^{-1} and 83 cm^{-1}, respectively. Evidently bond angles, the number of coordinating groups, cation

Table 20. Variation of U-O asymmetric stretching frequency (ν_3) with TOPO/U ratio

Ratio, TOPO/U	ν_3, cm^{-1}
8	930
4	931
2.67	931
2	931
1.6	932

charge and complex strength are all very important in determining the frequency shift values.

HDPM One band with two shoulders was observed for solutions containing HDPM in excess of that needed to form the disolvated uranium(VI) complex (Figure 18). The main band was observed at 1118 cm^{-1} while the shoulders were at 1108 cm^{-1} and 1080 cm^{-1}. The absorbance data for the band at 1118 cm^{-1} seemed to indicate that it was caused by the disolvated complex, $UO_2(NO_3)_2 \cdot 2HDPM$ (Figure 19). The shoulders located at 1108 cm^{-1} and 1080 cm^{-1} may have been caused by addition of the absorbances of the main complex band and the two small bands located at these points in the spectrum of 0.08 M HDPM (Figure 18). The lower frequency shoulder appeared to be explained by this reasoning because its absorbance changed very little with varying HDPM/U ratios. The absorbance data for the shoulder at 1108 cm^{-1} did show a change in slope very close to a 3:1 HDPM/U ratio and, coupled with the slope of 2.65 obtained for the partition data (Figure 14), the possibility of a trisolvated complex cannot be overlooked.

The absorbance of the band ascribed to the disolvated complex decreased and a new band was noted at 1136 cm^{-1} (Figure 18) when the HDPM/U ratio was decreased below 2:1. The data (Figure 19) supported identification of this band with the monosolvated complex $UO_2(NO_3)_2 \cdot HDPM$.

Saturation of 1,2-dichloroethane solutions of HDPM with

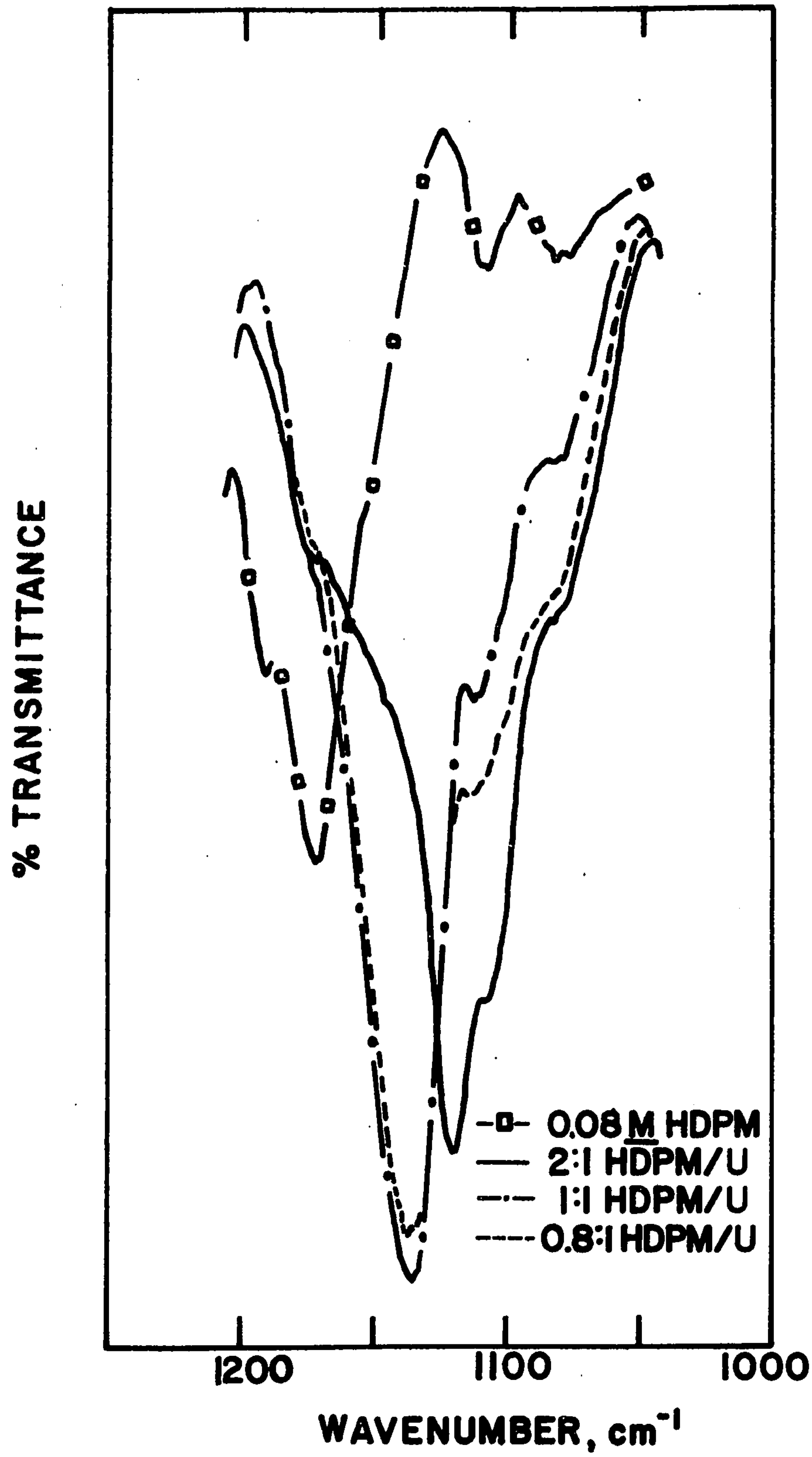


Figure 18. Uncomplexed and complexed phosphoryl spectra of HDPM and $UO_2(NO_3)_2 \cdot \nu HDPM$

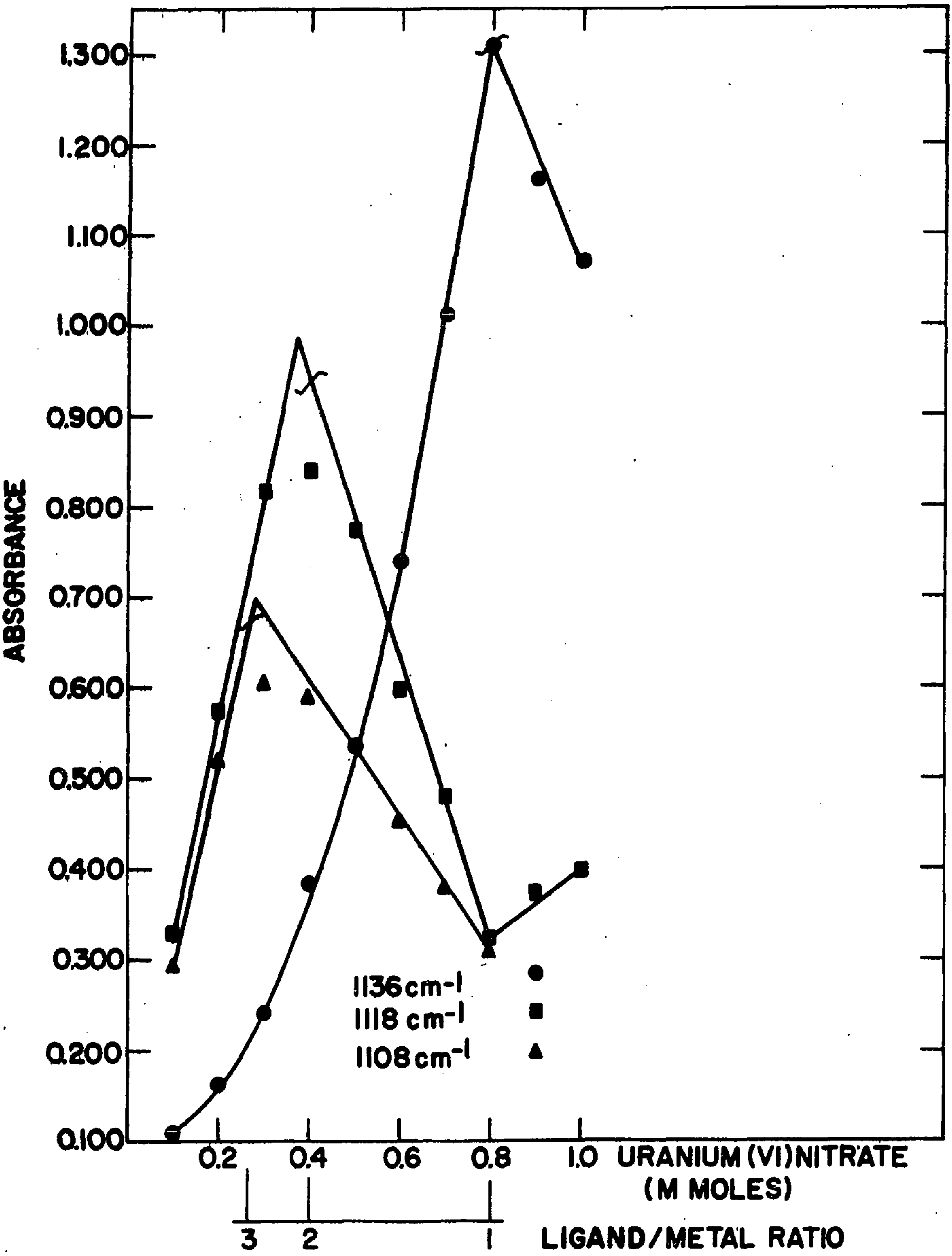


Figure 19. Absorbance of the complexed phosphoryl bands of uranium(VI) nitrate complexes of HDPM

$UO_2(NO_3)_2 \cdot 2H_2O$ gave a HDPM/U ratio of 0.84:1 (Table 18). This would seem to indicate a slight tendency toward formation of the hemisolvated bidentate complex, $2UO_2(NO_3)_2 \cdot HDPM$ by analogy with TOPO.

The band due to the asymmetric stretching mode of the U-O bond (ν_3) shifted 6.5 cm^{-1} toward higher frequencies on decreasing the HDPM/U ratio from 2:1 to 1.6:1 (Table 21). This indicated a sudden decrease in electron density around the uranium atom and a resultant increase in the U-O bond order. This would be expected on passing from a disolvated chelate with four phosphoryl oxygens coordinated to uranium to a monosolvated chelate with two phosphoryl oxygens coordinated.

Infrared spectra of solutions which had been dried with molecular sieves were completely devoid of the 1620 cm^{-1} hydroxyl bending mode of water for HDPM/U ratios greater than one. This band was observed for dried solutions in which the

Table 21. Variation of U-O asymmetric stretching frequency (ν_3) with HDPM/U ratio

Ratio, HDPM/U	ν_3, cm^{-1}
8	925
4	925.5
2.67	926.5
2	927.5
1.6	934
1.33	935
1.14	936
1	937.5
0.89	938

HDPM/U ratio was less than one. These data were interpreted as indicating the absence of water from the coordination sphere of the monosolvated and disolvated HDPM chelates. This was confirmed by Karl Fischer titration of the monosolvated complex.

HDPE A single complexed P-O band at 1108 cm^{-1} (Figure 20) was observed for HDPE/U ratios of eight through two inclusively. This may indicate that only one complex is present over this ligand/metal range. The absorbance data for this band (Figure 21) indicated that it was identified with the disolvated complex, $UO_2(NO_3)_2 \cdot 2HDPE$. The asymmetric stretching frequency (ν_3) of the U-O bond showed the same sudden increase in frequency (6.5 cm^{-1}) as occured for HDPM when the HDPE/U ratio was decreased from 2 to 1.6 (Table 22). This indicated a decrease in electron density similar to that observed for HDPM and thus a bidentate chelate structure seems logical for HDPE.

Table 22. Variation of U-O asymmetric stretching frequency (ν_3) with HDPE/U ratio

Ratio, HDPE/U	ν_3, cm^{-1}
8	922.5
4	923
2.67	924
2	925.5
1.6	932
1.33	934
1.14	934
1	935
0.89	935

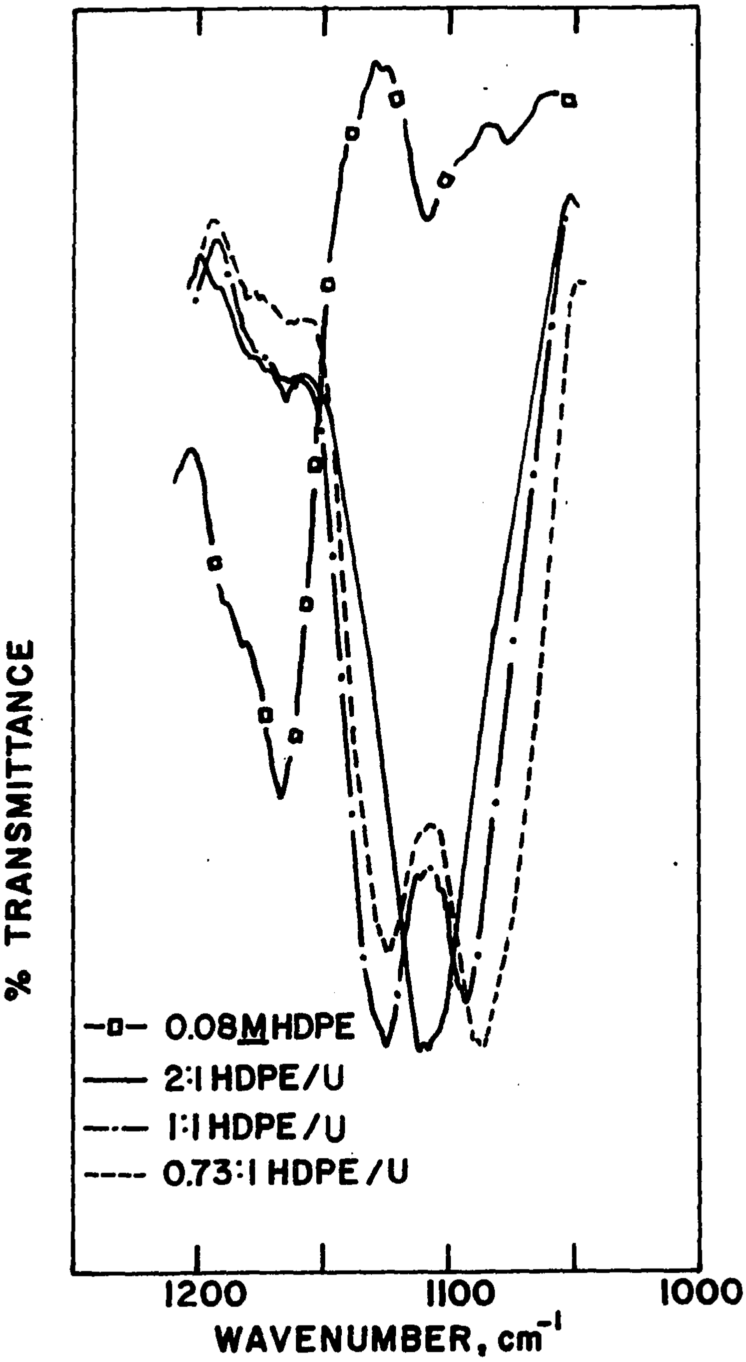


Figure 20. Uncomplexed and complexed phosphoryl spectra of HDPE and $UO_2(NO_3)_2 \cdot \nu HDPE$

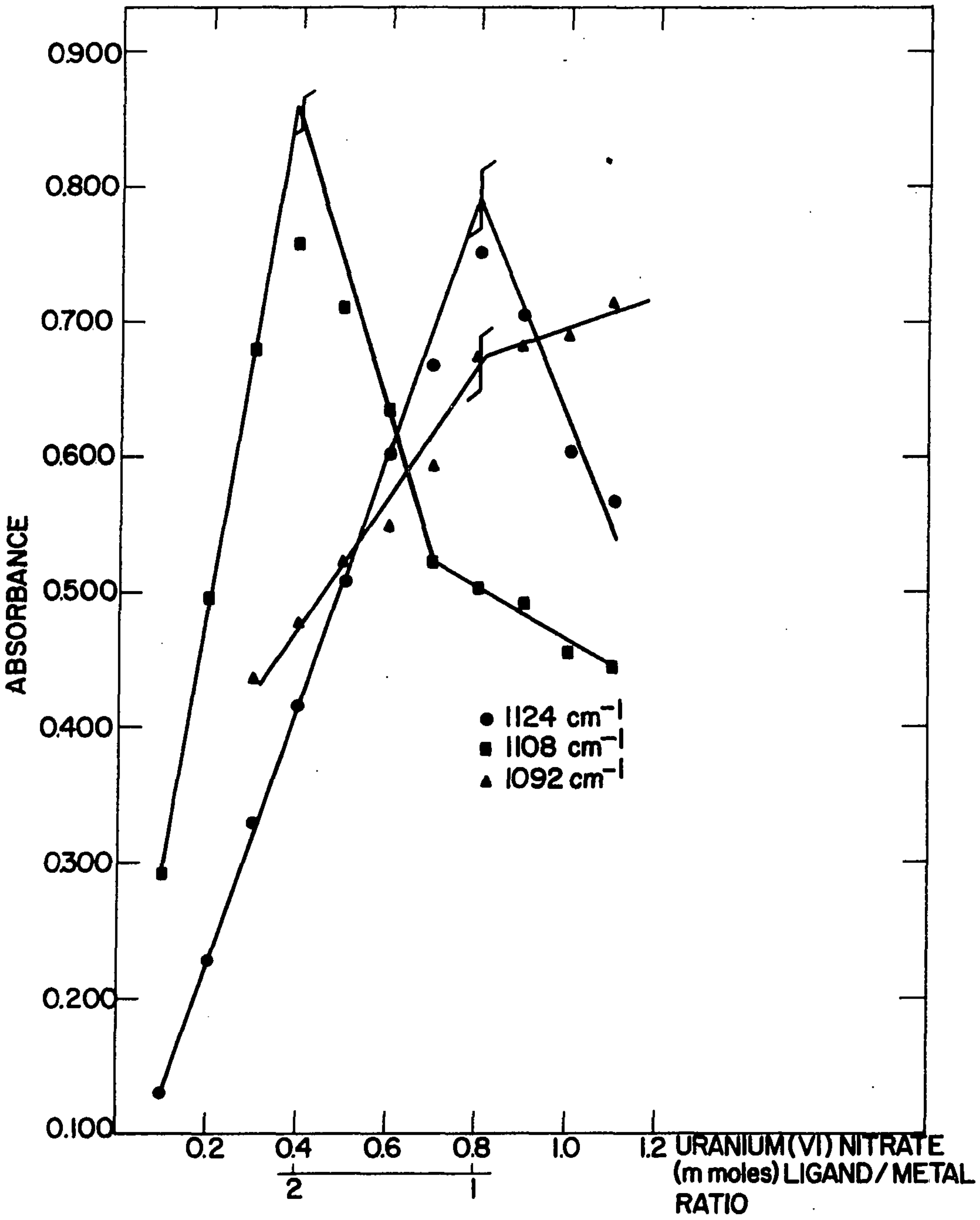
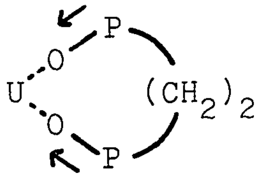


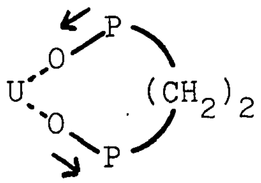
Figure 21. Absorbance of the complexed phosphoryl bands of uranium(VI) nitrate complexes of HDPE

Decreasing the HDPE/U ratio from 2 to 1.6 caused the band at 1108 cm^{-1} to decrease in intensity and the subsequent growth of two new bands, one on the high frequency side (1124 cm^{-1}) and one on the low frequency side (1092 cm^{-1}) of the band for the 2:1 complex (Figure 20). The absorbance data for these bands (Figure 21) indicated that they were both due to the monosolvated chelate, $UO_2(NO_3)_2 \cdot$HDPE. The band at 1092 cm^{-1} increased while the band at 1124 cm^{-1} decreased in intensity when the HDPE/U ratio was decreased from one to 0.89. This was probably caused by partial formation of the hemisolvated bidentate complex, $2UO_2(NO_3)_2 \cdot$HDPE. The loading capacities obtained for 1,2-dichloroethane solutions indicated that the formation of this complex had occurred to a greater extent for HDPE (HDPE/U-0.75) than for HDPM (HDPM/U-0.84) (Table 18). Increased separation between the active groups of the molecule would be expected to increase the probability of each phosphoryl group acting independently and thus causing the formation of increased amounts of the hemisolvated bidentate complex.

All evidence presented thus far strongly indicates that, at least in the monosolvated complex, both phosphoryl groups are coordinated to uranium for both HDPM and HDPE. Assuming bidentate chelate coordination of HDPE, two possibilities can be advanced to explain the splitting observed for the infrared band due to this complex. Changing dipole moments would be introduced into the molecule by the simultaneous movement of both phosphoryl oxygens toward uranium and also the movement of one oxygen toward uranium while the other one moves away as illustrated by I and II, respectively. This would lead to band splitting with I representing the symmetric stretching



I



II

frequency and II, the asymmetric stretching frequency. The second possible reason for band splitting is nonequivalent interaction of the two phosphoryl oxygens with the uranium atom. The more strongly interacting phosphoryl oxygen would be identified with the lower frequency band (1092 cm^{-1}) and the more weakly interacting one with the higher frequency band (1124 cm^{-1}).

Assignment of symmetric and asymmetric stretching modes for the monosolvated chelate does not appear to be justified as an explanation of the splitting observed for the band due to this complex since the disolvated chelate in which both ligands appear to be bidentate (evidence for this conclusion is shown in the section on the anion), has only a single band. This band would also have been split into two bands since this complex should exhibit four different stretching modes, two of which would be infrared active. The absence of splitting in the case of the disolvate tended to obviate assignment of asymmetric and symmetric stretching modes as a reasonable explanation for the splitting observed for the monosolvated chelate.

Nonequivalent bonding of the two phosphoryl oxygens appeared to be the most tenable explanation from the available evidence. The more strongly bonded phosphoryl group, represented by the low frequency band (1092 cm^{-1}), was observed to increase in intensity while the high frequency band (1124 cm^{-1}) decreased in intensity when the ligand/metal ratio was reduced below one. This was caused by formation of some of the hemisolvated bidentate complex, $2UO_2(NO_3)_2 \cdot HDPE$ as only a slight decrease in frequency was expected for the band due to this complex because it appeared that water replaced the departed phosphoryl group in the coordination shpere of uranium. The low frequency band was observed to shift from 1092 cm^{-1} to 1085 cm^{-1} in a stepwise manner as the HDPE/U ratio was decreased from 1 through 0.73 in the same manner.

The absence of splitting of the band identified with the monosolvated HDPM chelate is explained by the inflexibility of the active portion of the molecule caused by the single methylene bridge carbon. If both oxygens are to interact with uranium at all, they must react as a unit because of their proximity to each other and the more or less rigid structure within which they are held by the steric requirements of the alkyl chains attached to phosphorus. Therefore it is postulated that the two phosphoryl oxygens cannot interact nonequivalently with uranium in the case of HDPM.

The absence of nonequivalent bonding for the disolvated chelate, $UO_2(NO_3)_2 \cdot 2HDPE$ is explained by considering the electron density around uranium. With the wealth of electron density provided by the presence of four phosphoryl oxygens, the coordination requirements of the uranium atom should be able to be satisfied from greater distances. This factor and the stability gained by formation of a symmetric molecule suggested equivalent interaction for all four oxygens thus causing the appearance of only one infrared band for this complex.

HDPP One strong band (1085 cm^{-1}) with a shoulder on the high frequency side (1109 cm^{-1}) and a low intensity band at a higher frequency (1141 cm^{-1}) were observed for HDPP (Figure 22). The absorbance data (Figure 23) indicated that the shoulder at 1109 cm^{-1} was identified with a monosolvated complex and the small band at 1141 cm^{-1} was identified with a disolvated complex. The strong band at 1085 cm^{-1} underwent several changes in slope but could not be definitely identified with any particular complex. The intensity increase observed for this band when the ratio HDPP/U was decreased below one was very similar to the behavior of the low frequency band of the doublet observed for the monosolvated complex of HDPE. Thus, by analogy this band may be the other half of a doublet

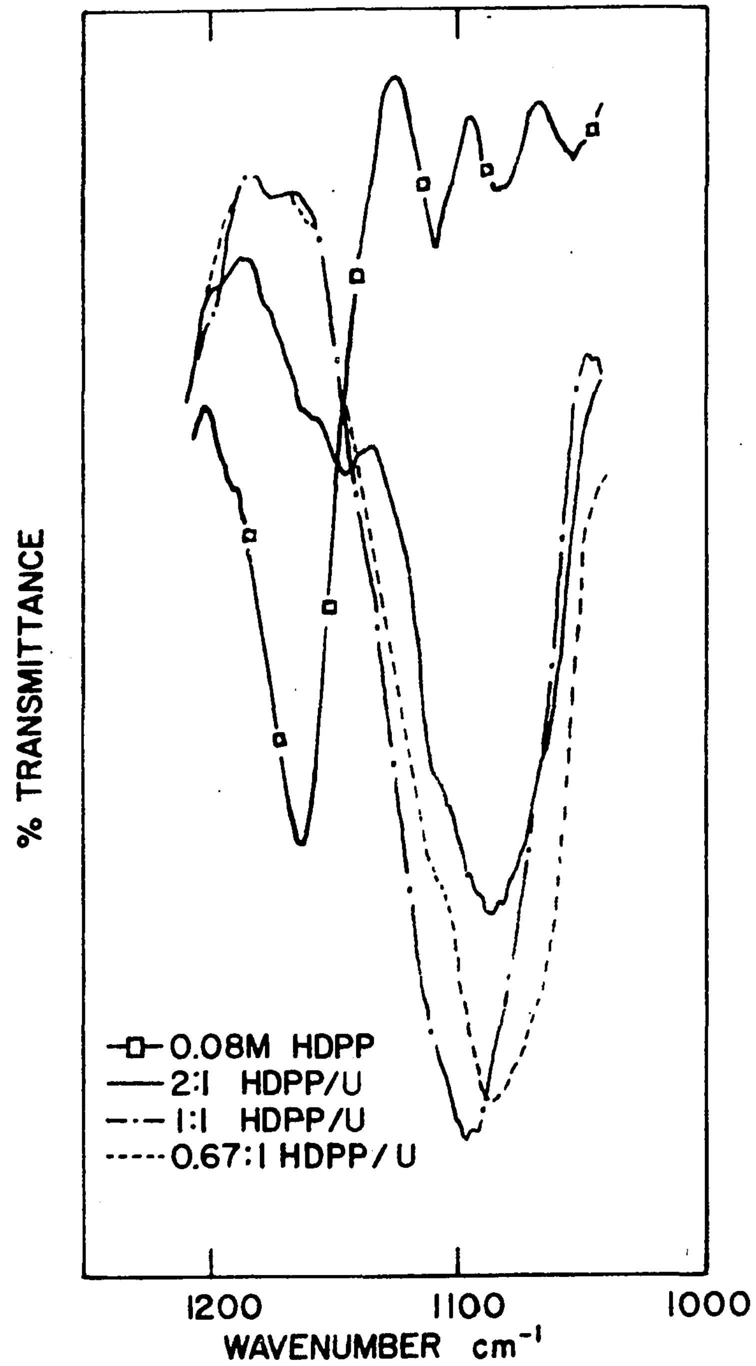


Figure 22. Uncomplexed and complexed phosphoryl spectra of HDPP and $UO_2(NO_3)_2 \cdot \nu HDPP$

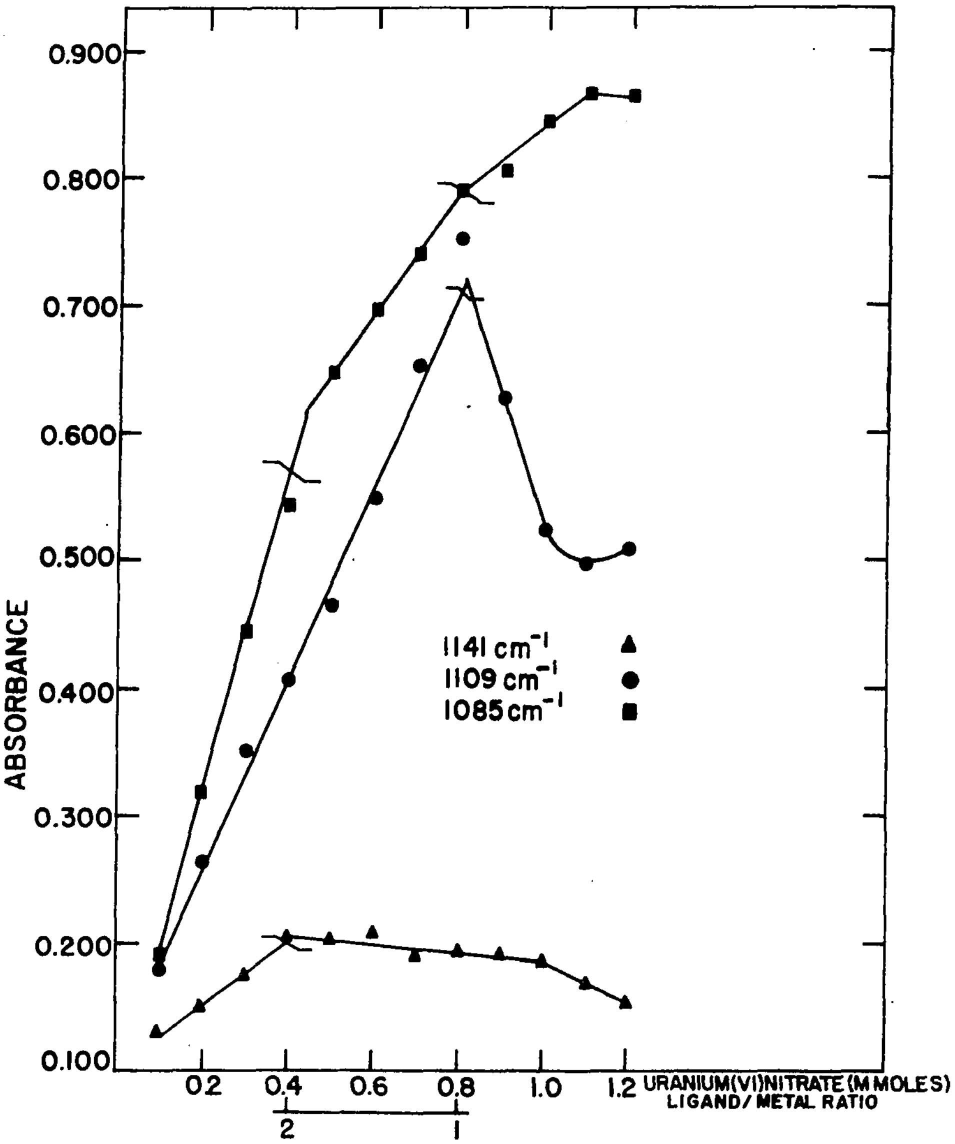


Figure 23. Absorbance of the complexed phosphoryl bands of uranium(VI) nitrate complexes of HDPP

for the monosolvated chelate, $UO_2(NO_3)_2 \cdot HDPP$. Saturation of 1,2-dichloroethane solutions of HDPP with uranium(VI) nitrate dihydrate produced a ratio, HDPP/U, of 0.68 (Table 18). This may explain the lack of a break in the absorbance versus mole-ratio curve for the 1085 cm^{-1} band (Figure 23) as it indicated considerable formation of the hemisolvated bidentate complex, $2UO_2(NO_3)_2 \cdot HDPP$. This would lead to a continual increase in the absorbance of the low frequency band and thus fail to give a sharp change in slope.

The frequency of the 1085 cm^{-1} band varied in a peculiar manner with changes in the ratio HDPP/U. Table 23 indicates the variation in the maximum of this band as a function of this ratio. Corresponding changes occurred in the nitrate frequencies and a possible explanation of these changes will be advanced in the section on the state of the nitrate anion.

Table 23. Variation in frequency of the maximum of the complexed phosphoryl band (1085 cm^{-1})

Ratio, HDPP/U	Frequency, cm^{-1}
1.6	1087
1.33	1087
1.14	1093
1	1096
0.89	1091
0.80	1086

A positive statement about the absence of water from the coordination sphere of uranium cannot be made for the monosolvate of HDPP as the band due to the hydroxyl bending mode did not completely disappear for dried solutions with HDPP/U ratios near one. The decrease in absorbance was rather irregular and probably indicated that the solutions were not equilibrated with the molecular sieves for sufficient time to allow complete drying of the solutions.

The U-O asymmetric stretching frequency (ν_3) did not exhibit the rather sharp increase in frequency on decreasing the HDPP/U ratio below two as was the case for HDPM and HDPE. An increase in frequency was observed with decreasing HDPP/U ratios but it was only slight and rather gradual (Table 24). This seemed to indicate the absence of any sudden change in electron density around the uranium atom.

Table 24. Variation of U-O asymmetric stretching frequency (ν_3) with HDPP/U ratio

Ratio, HDPP/U	ν_3, cm^{-1}
8	927
4	928.5
2.67	928.5
2	928.5
1.6	930
1.33	931
1.14	931
1	931
0.89	931

The slopes of the partition data for HDPP (Figure 14, 15) were found to be non-integral in value. The infrared data indicated the presence of a disolvated complex but it appeared to be of rather low stability. Thus, the slope data are probably best interpreted as indicating a mixture of the monosolvated chelate, $UO_2(NO_3)_2 \cdot HDPP$, and the disolvated complex, $UO_2(NO_3)_2 \cdot 2HDPP$.

<u>HDPB</u> The uranium-complexed phosphoryl bands of HDPB were very similar in appearance to those of HDPP (compare Figure 22 and 24) although they were not all identified with the same complexes as obtained for HDPP.

The band appearing as a shoulder at 1110 cm^{-1} and the low intensity band at 1134 cm^{-1} (Figure 24) were both identified with the monosolvated chelate, $UO_2(NO_3)_2 \cdot HDPB$ (Figure 25). The absorbance of the strong band at 1084 cm^{-1} changed slope sharply at a HDPB/U ratio of 1.5 (Figure 25). The intensity of this band decreased initially after the slope change and then increased. Partial formation of a hemisolvated bidentate complex, $2UO_2(NO_3)_2 \cdot HDPB$, was indicated by analysis of 1,2-dichloroethane solutions of HDPB saturated with uranium(VI) nitrate dihydrate. The ratio, HDPB/U, observed for this organophosphorus compound was identical (0.68) (Table 18) with that obtained for HDPP. This would explain the increased intensity exhibited by the band at 1084 cm^{-1} as the HDPB/U ratio was decreased below one. A reasonable explanation linking this

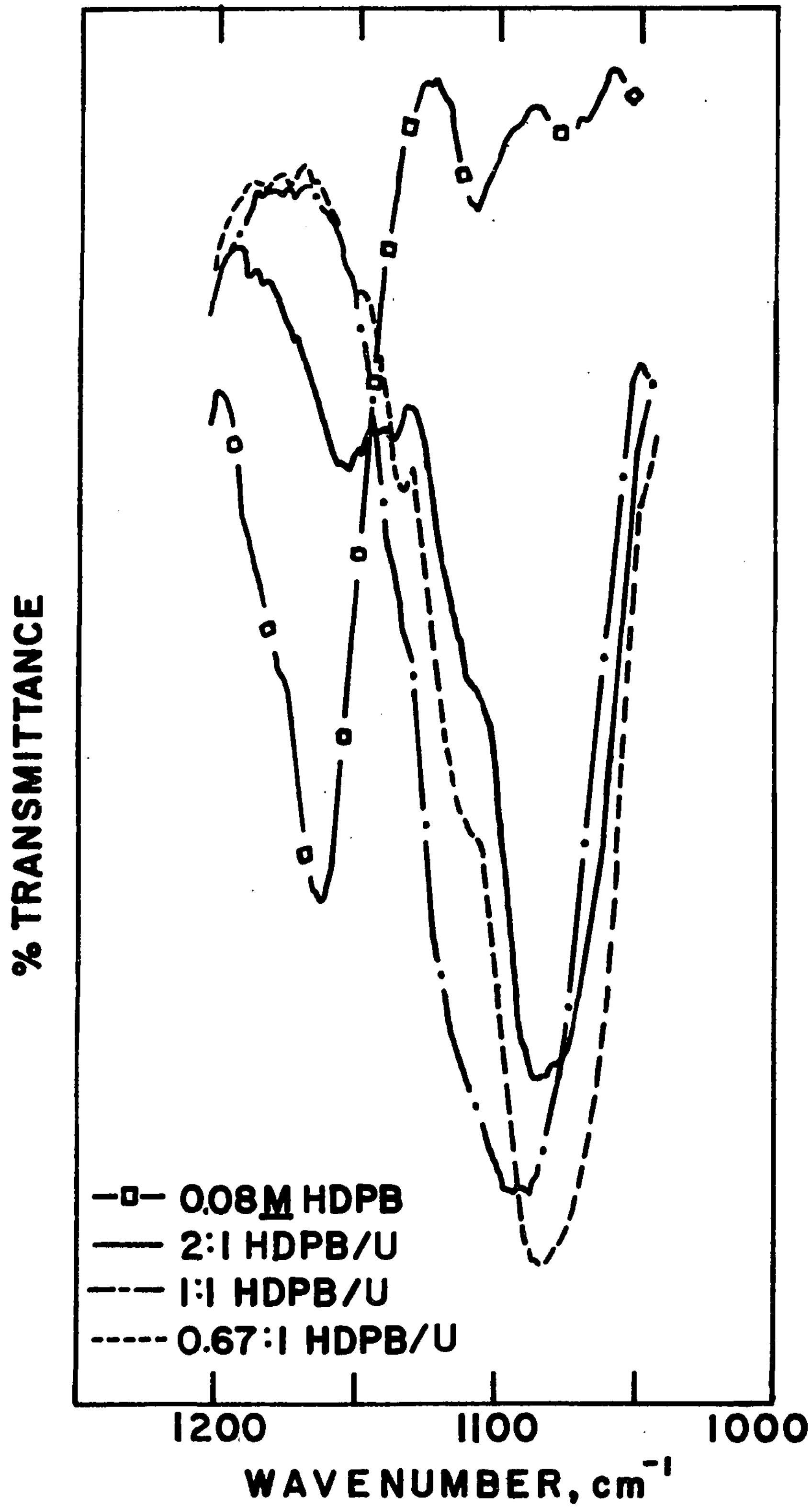


Figure 24. Uncomplexed and complexed phosphoryl spectra of HDPB and $UO_2(NO_3)_2 \cdot \nu HDPB$

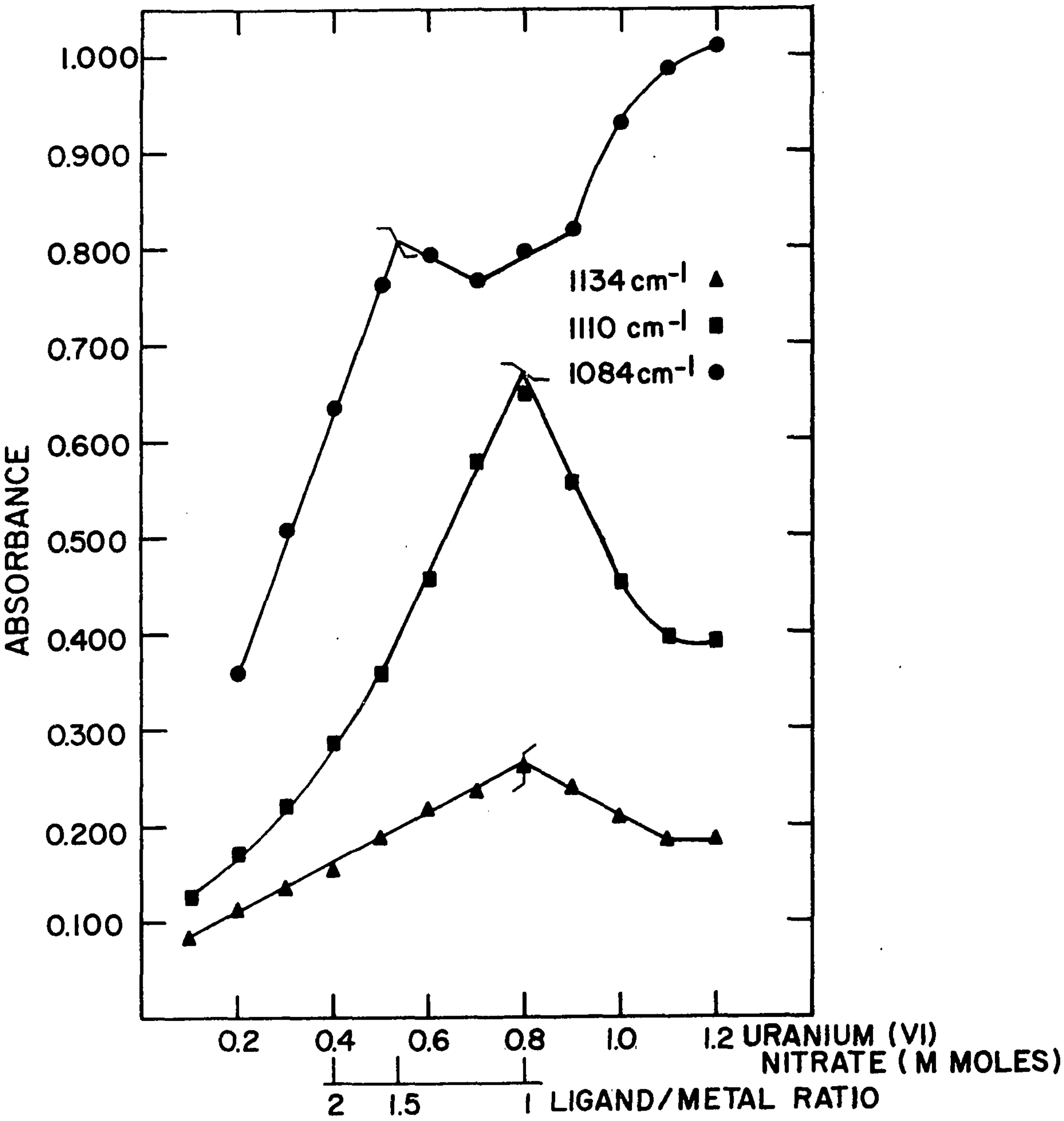


Figure 25. Absorbance of the complexed phosphoryl bands of uranium(VI) nitrate complexes of HDPB

band, presumably caused by a sesquisolvated complex (indicated by the slope of Figure 15 and the absorbance data in Figure 25), with the hemisolvated bidentate complex can not be advanced from these spectral studies.

The hydroxyl bending mode of water at 1620 cm^{-1} was not observed in the spectra of HDPB-uranium solutions which had been dried with molecular sieves if the ligand/metal ratio was equal to or greater than one. When the ligand/metal ratio was decreased below one, this band was observed. These data were interpreted as indicating that the monosolvated chelate, $UO_2(NO_3)_2 \cdot HDPB$, was anhydrous while the uranium atom of the hemisolvated bidentate complex probably contained water in its coordination sphere.

A shift to higher frequencies, similar but smaller in magnitude than that observed for the band at 1085 cm^{-1} of the HDPP complex (Table 22), was noted for the band of the HDPB complex at 1084 cm^{-1} (Table 25). Discussion of this shift will be deferred until the section on the state of the anion.

The frequency change of the asymmetric stretching band (ν_3) of the HDPB-uranium complexes was similar to results obtained for HDPP (Table 23). Only a small, steady increase in the U-O asymmetric frequency (ν_3) was noted as the HDPB/U ratio was decreased (Table 26) and thus no sudden large decrease in electron density around the uranium atom was indicated by the data.

Table 25. Variation in frequency of the maximum of the complexed phosphoryl band (1084 cm^{-1})

Ratio, HDPB/U	Frequency, cm^{-1}
1.6	1085
1.33	1087
1.14	1088
1	1088-1098(broad)
0.89	1088
0.80	1086
0.67	1084

Table 26. Variation of U-O asymmetric stretching frequency (ν_3) with HDPB/U ratio

Ratio, HDPB/U	ν_3, cm^{-1}
8	929.5
4	929.5
2.67	930
2	930
1.6	931
1.33	932
1.14	932
1	933.5
0.89	933.5

The frequency data of the U-O asymmetric stretching band for the uranium complexes of HDPP and HDPB were distinctly different from the data for HDPM and HDPE. The frequency of this band for the complexes of TOPO, HDPP and HDPB (Tables 20, 24, 25) indicated that, at high ligand/metal ratios, the U-O bond of the UO_2^{+2} ion had a higher bond order than this bond exhibited in the higher complexes of HDPM and HDPE (Tables 21, 22). This may be indicative of higher electron density around the uranium atom for the latter complexes.

Absorbance of the uncomplexed phosphoryl band in the infrared

The absorbance of the free phosphoryl band is proportional to the concentration of this bond as shown by the Beer-Lambert law,

$$A = \epsilon l C_{P-O}$$

where ϵ = molar absorptivity coefficient (liter/mole-cm), l = path length (cm) and C_{P-O} = concentration of phosphoryl bond in moles/liter. The quantity ϵ is a constant and the path length was maintained constant during these infrared investigations, therefore, the concentration of P-O bond can be written as shown in Equation 12.

$$C_{P-O} = A/k \tag{12}$$

The reaction between uranium(VI) nitrate and a organophosphorus reagent, is described by the following reaction,

$$UO_2^{+2} + 2NO_3^{-1} + \nu S \longrightarrow UO_2(NO_3)_2 \cdot \nu S$$

where ν is the solvation number. Thus the concentration of uncomplexed P-O bond will be a function of the concentration of uranium(VI) nitrate with the slope representing the solvation number if a single complex is formed and all phosphoryl groups of the molecule are coordinated. Figures 26 and 27 contain absorbance data for the uncomplexed phosphoryl bands of the five organophosphorus compounds as a function of the amount of uranium(VI) nitrate present. The data presented in the figures are the absolute absorbances of the regions in question since the infrared spectrometer was balanced at 100% transmittance for a scan of solvent versus solvent in the uncomplexed phosphoryl band absorbance region.

The solvation number was determined for TOPO (Figure 26) by extrapolation of the linear portion of the curve to zero absorbance. The amount of uranium obtained for this intercept divided by the known amount of TOPO present gave ν, the solvation number. A value of 1.9 was obtained for TOPO which was reasonably close to the expected value of 2 for the disolvated complex. The spectra indicated that the concentration of the trisolvated complex was small and thus it would not be expected to affect the slope, especially after the initial addition of uranium.

It was not possible to determine a solvation number for the bidentate organophosphorus compounds from these data because it appeared that another band was present under the free phosphoryl band or else a new band was growing at the same rate as the uncomplexed band was decreasing. Other complications were introduced by the presence of mixtures of complexes

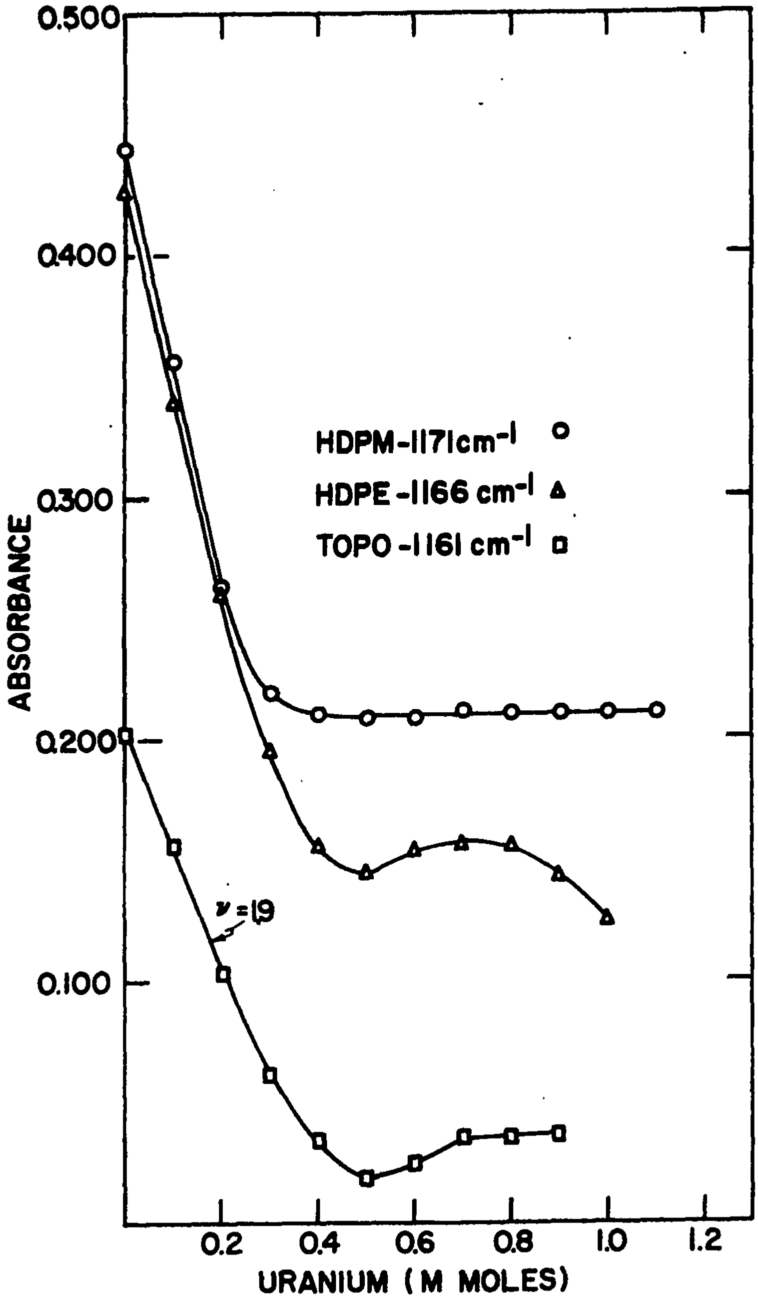


Figure 26. Variation in absorbance of uncomplexed phosphoryl bands with increasing uranium(VI) nitrate concentration (organophosphorus compound-0.8 mmoles)

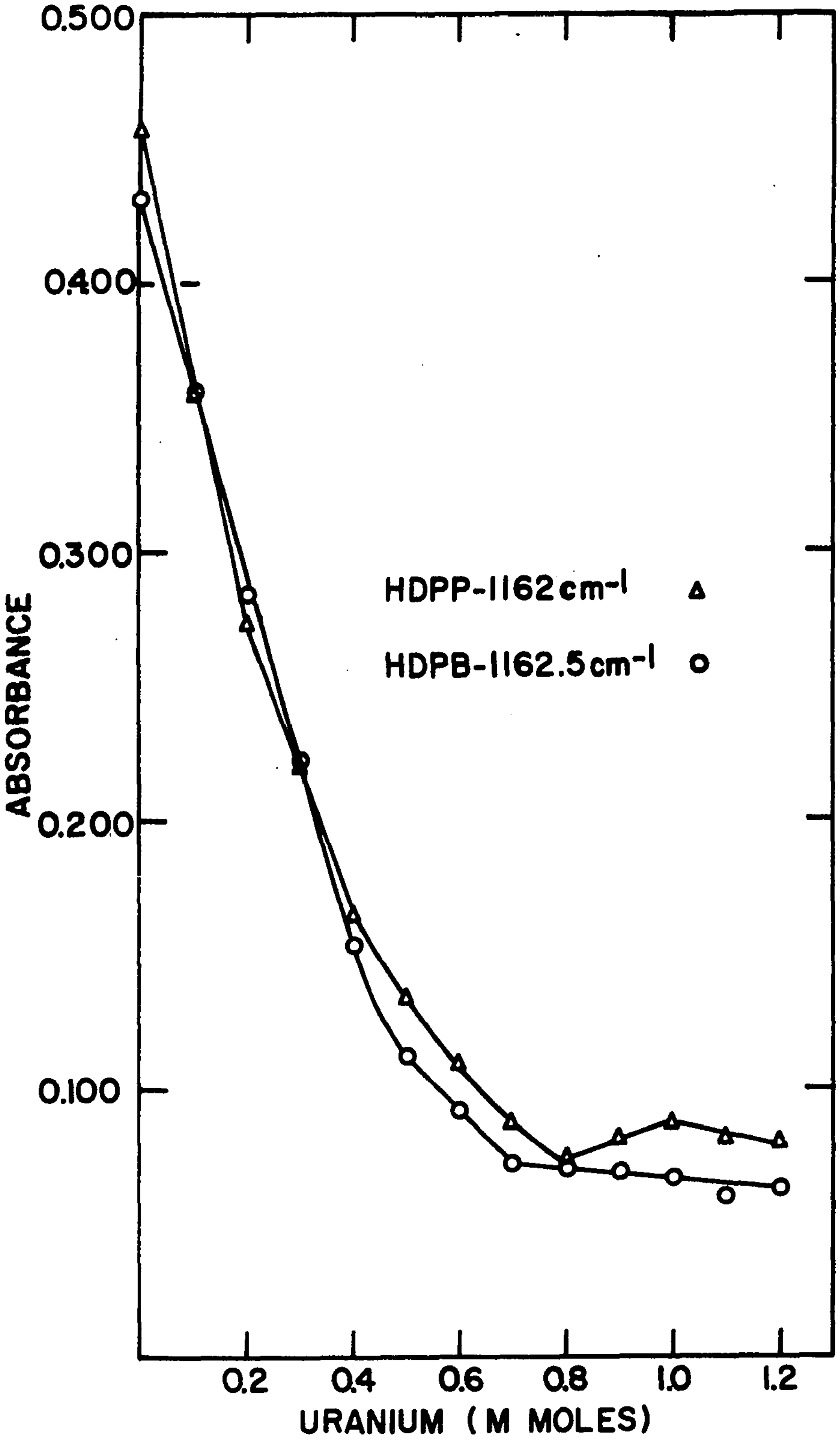
and the fact that all phosphoryl groups were not bonded to uranium for the higher complexes of HDPP and HDPB. Qualitatively it appeared as though the decrease in free phosphoryl absorbance leveled off at a 2:1 ratio for HDPE while it leveled off between a 3:1 and a 2:1 ratio for HDPM. The absorbance of the free phosphoryl band continued to decrease until a 1:1 ligand/metal ratio was attained for HDPP and HDPB (Figure 27).

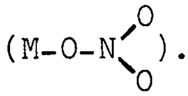
Infrared investigation of the state of the nitrate anion

The role of the anion was quite important in determining whether the organophosphorus compounds were reacting as monodentate or bidentate ligands. The nature of the nitrate and the alteration of its coordination properties with varying ligand/metal ratios were investigated by observation of the infrared spectra which were interpretated according to the background data of Tables 1, 2 and 3. The presence of ionic nitrate, shown by the appearance of a band at 1350 cm^{-1}, signified that the organophosphorus ligand had satisfied the coordination requirements of uranium and displaced nitrate from the coordination sphere when the ligand was present in excess of a 1:1 ligand/metal ratio.

The appearance of the asymmetric stretching (ν_4) and the symmetric stretching (ν_1) frequencies of the C_{2v} nitrato group (Table 3) indicated that the coordination of nitrate to the uranium atom had occured. This signified that the ligand alone

Figure 27. Variation in absorbance of uncomplexed phosphoryl bands with increasing uranium(VI) nitrate concentration (organophosphorus compound-0.8 mmoles)


0.500
0.400
0.300
0.200
0.100
ABSORBANCE
0.2
0.4
0.6
0.8
1.0
1.2
URANIUM (M MOLES)
HDPP-1162 cm-1 △
HDPB-1162.5 cm-1 ○

was unable to satisfy the coordination requirements of the uranium atom. Katzin, after a survey of the spectra of a number of metal nitrates, reported that a splitting, $\Delta(\nu_4 - \nu_1)$ in excess of 125 cm^{-1} definitely indicated a coordinated nitrato group  $(\mathrm{M{-}O{-}N}\begin{smallmatrix}\diagup \mathrm{O}\\ \diagdown \mathrm{O}\end{smallmatrix})$. Metal nitrates having splitting values between 90-125 cm^{-1} could not be assigned definitely as having either covalent or ionic nitrate and anything lower than 90 cm^{-1} represented merely electrostatic or second-sphere effects (57). Splitting values were generally greater than 125 cm^{-1} for the complexes of uranium(VI) nitrate and HDPE, HDPP, HDPB and TOPO.

Allpress and Hambly (4) reported infrared spectral data of various hydrates of uranium(VI) nitrate. Their data showed differences in the degree of covalency of the nitrate (represented by $\Delta(\nu_4 - \nu_1)$) depending upon the hydration number (Table 27). Increasing values of $\Delta(\nu_4 - \nu_1)$ were calculated from their data with decreases in the hydration number. This was as expected since the oxygen of a water molecule can serve as a donor atom and a decrease in the number of donor atoms should result in increased covalency for the nitrato group. As the metal-oxygen interaction increases for the coordinated nitrato group, the oxygen-nitrogen bond order should decrease as signified by a decrease in the frequency of the N-O stretch (ν_2). This was observed as shown by the data of Allpress and Hambly (Table 27).

Table 27. Some nitrate frequencies of $UO_2(NO_3)_2 \cdot XH_2O$ (X = 2, 3, 6)

Band assignment	$UO_2(NO_3)_2 \cdot 6H_2O$	$UO_2(NO_3)_2 \cdot 3H_2O$	$UO_2(NO_3)_2 \cdot 2H_2O$
$\nu_4(ONO_2)$	1536 s 1497 s	1540 s 1506 s	1540 s
$\nu_1(ONO_2)$	1333 m 1297 m	1306 s 1276 s	1268 s
$\Delta(\nu_4 - \nu_1)$	164 239	200 266	272
$\nu_2(ONO_2)$	1042 m 1052 m	1032 m 1045 m	1029 s

$\nu_4(ONO_2)$-asym. NO_2 stretching
$\nu_1(ONO_2)$-sym. NO_2 stretching
$\nu_2(ONO_2)$- -O-N stretching

The infrared spectra covering the important nitrate and nitrato absorption regions are presented for the uranium(VI) nitrate complexes of HDPM, HDPE, HDPP, HDPB and TOPO (Figure 28, 30, 32, 34 and 36). The absorbance data for the asymmetric stretching frequency, $\nu_4(ONO_2)$, of the covalent nitrato group and the asymmetric stretching frequency, $\nu_3(NO_3^{-1})$, of the ionic nitrate group are presented following each spectrum (Figure 29, 31, 33, 35 and 37). The absorbance data for the asymmetric stretching frequency, ν_4, are intended to merely show the relative rate of increase of covalent nitrate and, since this band shifts slightly depending on covalency, the reading was taken at the point of maximum absorbance of the band. The frequencies of the three main nitrato bands (ν_4, ν_1, ν_2) are reported in Tables 28-32. Pairing of bands for the determination of splitting values, $\Delta(\nu_4 - \nu_1)$, was accomplished by pairing bands which exhibited similar intensity changes and were symmetrically located with respect to the asymmetric stretching frequency of the ionic nitrate group. Dashed values for $\Delta(\nu_4 - \nu_1)$ meant that one or the other band was not able to be definitely assigned or a broad band was present and it was not feasible to assign a splitting value. The absorbance of $\nu_3(NO_3^{-1})$, appearing at 1350 cm^{-1} for the complexes, was plotted against concentration of uranium(VI) nitrate (Figure 29, 31, 33, 35, 37) to show the rise and fall of ionic nitrate concentration and to locate the ligand/metal ratio at which the peak concentration was achieved.

The first increase in covalent nitrate concentration was very slow for HDPM and HDPE compared to the increases observed for HDPP, HDPB and TOPO (compare the initial slopes of ν_4 data of Figures 29 and 31 with those of Figures 33, 35 and 37). These data were interpreted as indicating the displacement of both nitrate groups from the coordination sphere of uranium by HDPM and HDPE and thus, assuming that uranium has four equatorial coordination positions, the disolvates of these compounds appear to have both ligands coordinated to the metal in chelate rings.

A sharp increase in splitting, $\Delta(\nu_4 - \nu_1)$, was noted for HDPE when the ligand/uranium ratio was decreased below one (Table 29). This indicated that the nitrato groups became more covalent than they were in the monosolvated chelate. This would appear to confirm formation of a hemisolvated bidentate complex, $2UO_2(NO_3)_2 \cdot HDPE$, since this complex, having only a single P-O group coordinated to uranium, would require increased covalency of the nitrato groups. The splitting observed for HDPM (Table 28) was only slightly increased but this can be explained by the difference in concentration of the hemisolvated bidentate complexes as shown by saturation studies (HDPM/U ratio-0.84; HDPE/U ratio-0.75) (Table 18). This explanation seemed to be confirmed by observation of the N-O stretching frequency, $\nu_2(ONO_2)$. A more highly covalent bond formed between the metal and the oxygen of the nitrato group would result in a decrease in the nitrogen-oxygen bond order which would cause the N-O stretching band, $\nu_2(ONO_2)$ to shift in the direction of lower frequencies. This was noted for HDPE (HDPE/U-0.80, Table 29) by a sharp increase in intensity and a decrease in frequency for the main band whereas the main band for HDPM remained stationary with only a shoulder appearing on the low frequency side of this band (HDPM/U-0.80, Table 28). This would appear to confirm the decreased splitting, $\Delta(\nu_4 - \nu_1)$, observed for HDPM as being due to a lower concentration

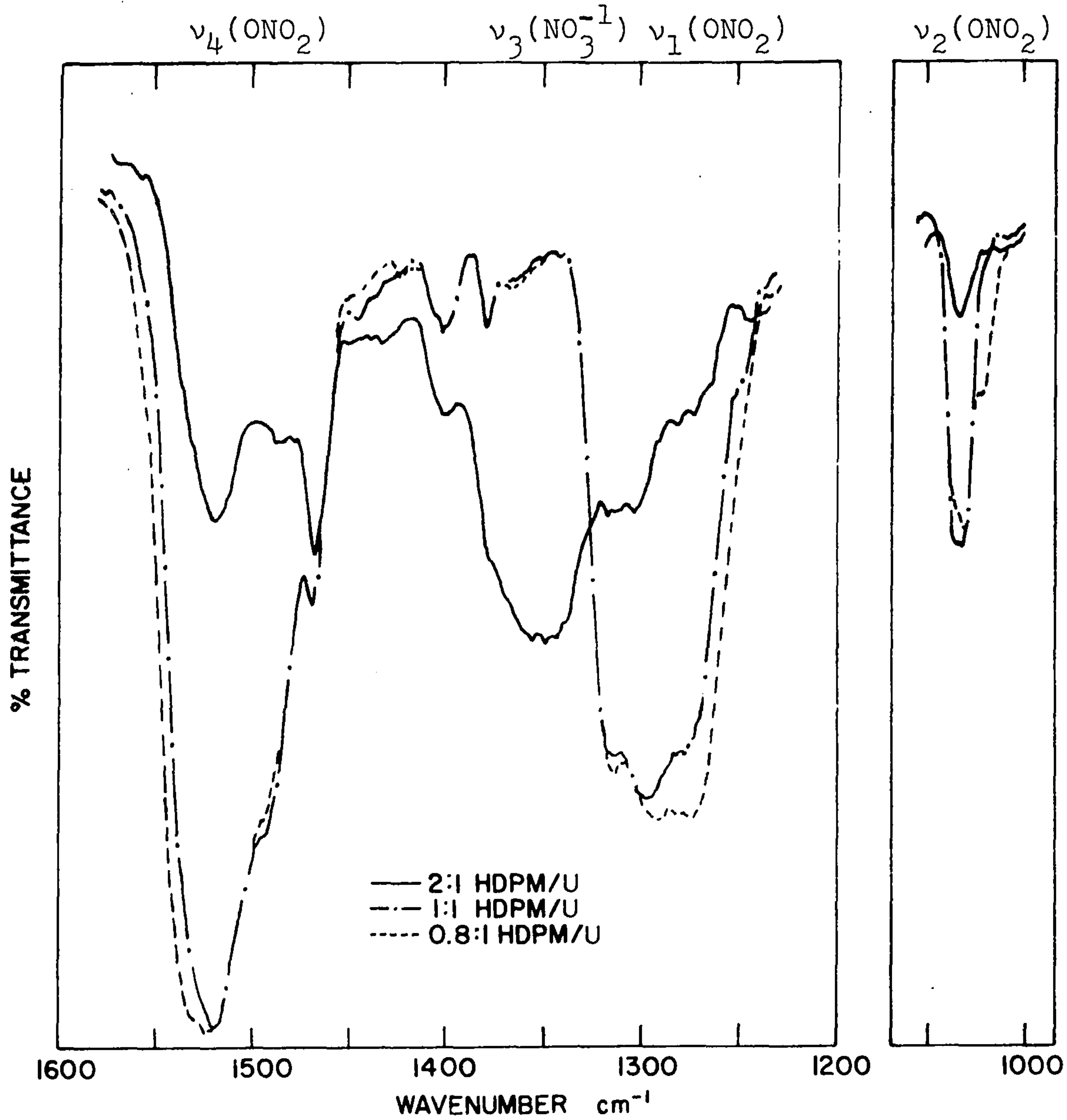


Figure 28. Spectra of covalent (ν_4, ν_1, ν_2) and ionic (ν_3) nitrate regions for uranium(VI) nitrate complexes of HDPM

Figure 29. Covalent (ν_4) and ionic (ν_3) nitrate bands of uranium(VI) nitrate complexes of HDPM

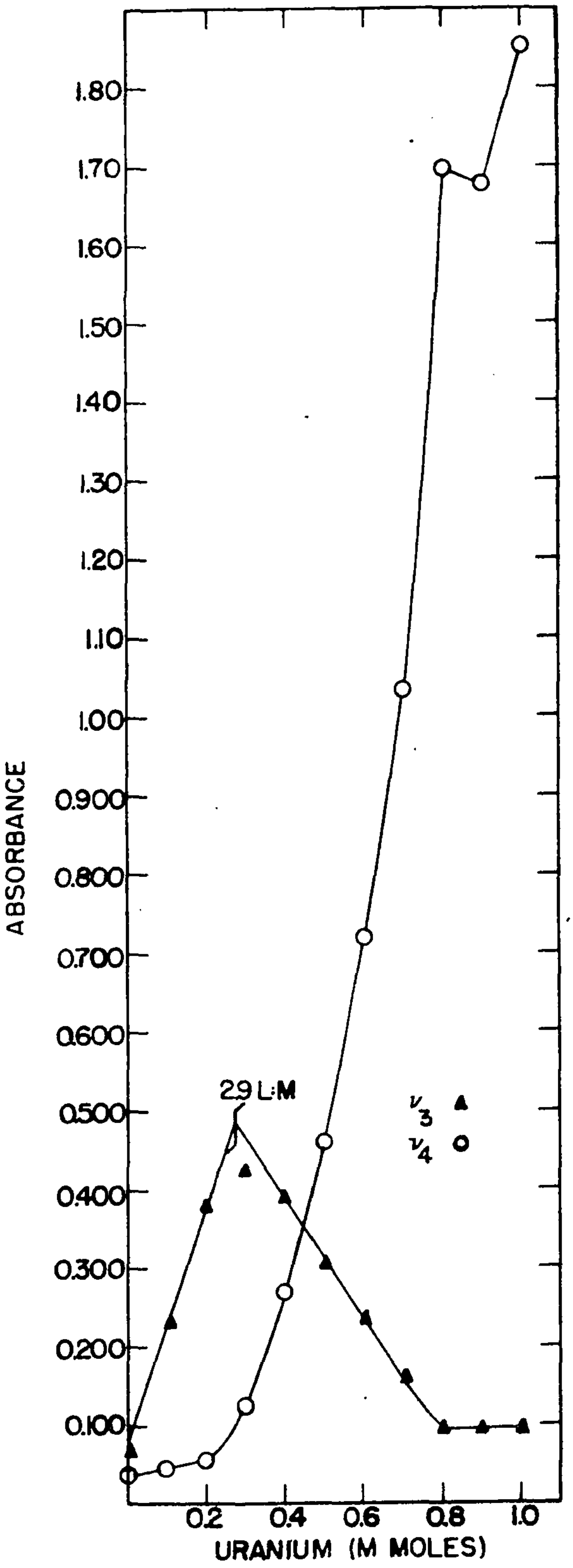

ABSORBANCE
1.80
1.70
1.60
1.50
1.40
1.30
1.20
1.10
1.00
0.900
0.800
0.700
0.600
0.500
0.400
0.300
0.200
0.100
2.9 L:M
ν_3 ▲
ν_4 ○
0.2
0.4
0.6
0.8
1.0
URANIUM (M MOLES)

Table 28. Frequency data for nitrato bands of $UO_2(NO_3)_2 \cdot \nu HDPM$

Ratio, HDPM/U	$\nu_4(ONO_2)$	$\nu_1(ONO_2)$	$\Delta(\nu_4 - \nu_1)$	$\nu_2(ONO_2)$
8	no bands	no bands		no bands
4	no bands	no bands		no bands
2.67	1519 bw	1306 w sh	-	no bands
2	1487 m sh	1312 b sh*	-	1033 m
	1520 s*	1278 m sh	242	
1.33	1495 m sh	1311 b sh*	184	1033 s
	1520 s*	1286 m sh	234	
1	1495 m sh	1315 m sh	180	
	1519 s*	1298 s*	221	1032 s
	sh	1279 m sh	-	
0.80	1495 m sh	1314 m sh	181	
	1519 s sh	1293 s sh*	226	1022 m sh
	1524 s*	1276 s sh*	248	1031 s*

w-weak, m-medium, s-strong, bw-broad weak, sh-shoulder, w sh-weak shoulder etc.

---

*Strongest band.

of the hemisolvated bidentate complex.

Ionic nitrate was observed in the presence of excess HDPP and HDPB as shown by the band at 1350 cm^{-1} (Figure 32, 34). The initial slopes observed for ν_4 (Figure 33, 35) indicated that covalent nitrate was increasing simultaneously with ionic nitrate but it appeared that the increase of covalent nitrate was more rapid for HDPB. The relative slopes were 1.3 for

Table 29. Frequency data for nitrato bands of $UO_2(NO_3)_2 \cdot \nu HDPE$

Ratio, HDPE/U	$\nu_4(ONO_2)$	$\nu_1(ONO_2)$	$\Delta(\nu_4 - \nu_1)$	$\nu_2(ONO_2)$
8	no bands	no bands		no bands
4	-- 1522 bw	1319 m sh* 1265-90 bw	-- --	--
2.67	-- 1520 bw	1315 m* 1265 b sh	-- --	1012-34 bw
2	1438 w sh 1522 s* 1526 s sh	1319 s* 1279 m sh 1268 m sh	119 243 258	1032 w
1.33	1454 w sh 1490 w sh 1517 s*	1316 s* 1304 b sh 1274 m sh	138 186 243	1032 s
1	1496 m sh 1518 s* --	1316 s sh 1298 s* 1278 m sh	180 220 --	1036 s
0.80	1496 w sh 1518 s sh 1532 s*	1316 m sh 1292 s* 1272 s sh	180 226 260	1030 m sh 1021 s*

w-weak, m-medium, s-strong, b-broad, sh-shoulder, bw-broad weak, w sh-weak shoulder, etc.

---

*Strongest band.

HDPP (average slope drawn through the first four points -ν_4, Figure 33) and 1.7 for HDPB. The initial increases in covalent nitrate concentration for these compounds were significantly greater than was observed for HDPM and HDPE (compare initial slopes of ν_4 data, Figures 29, 31, 33, 35). The slope

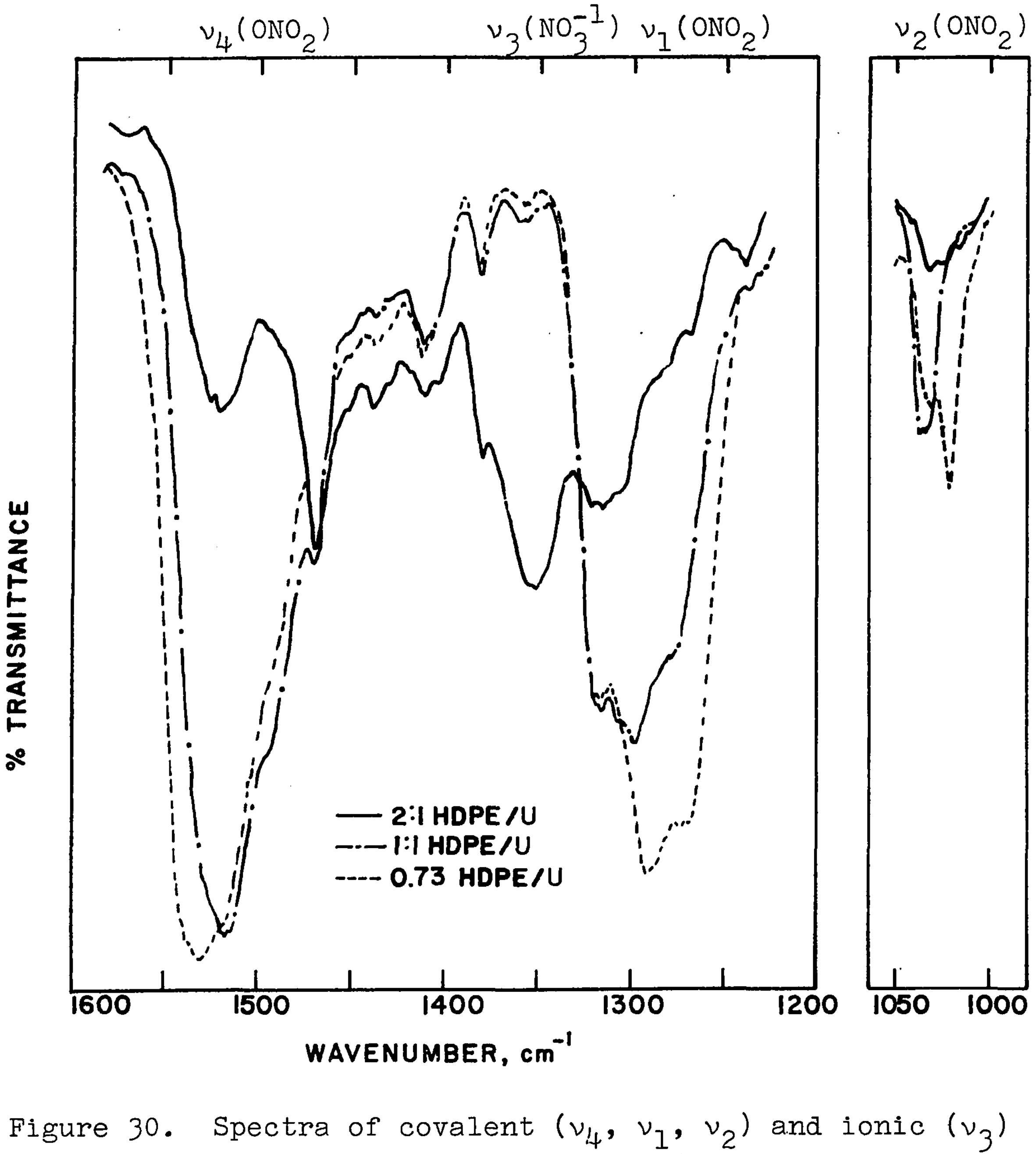


Figure 30. Spectra of covalent (ν_4, ν_1, ν_2) and ionic (ν_3) nitrate regions for uranium(VI) nitrate complexes of HDPE

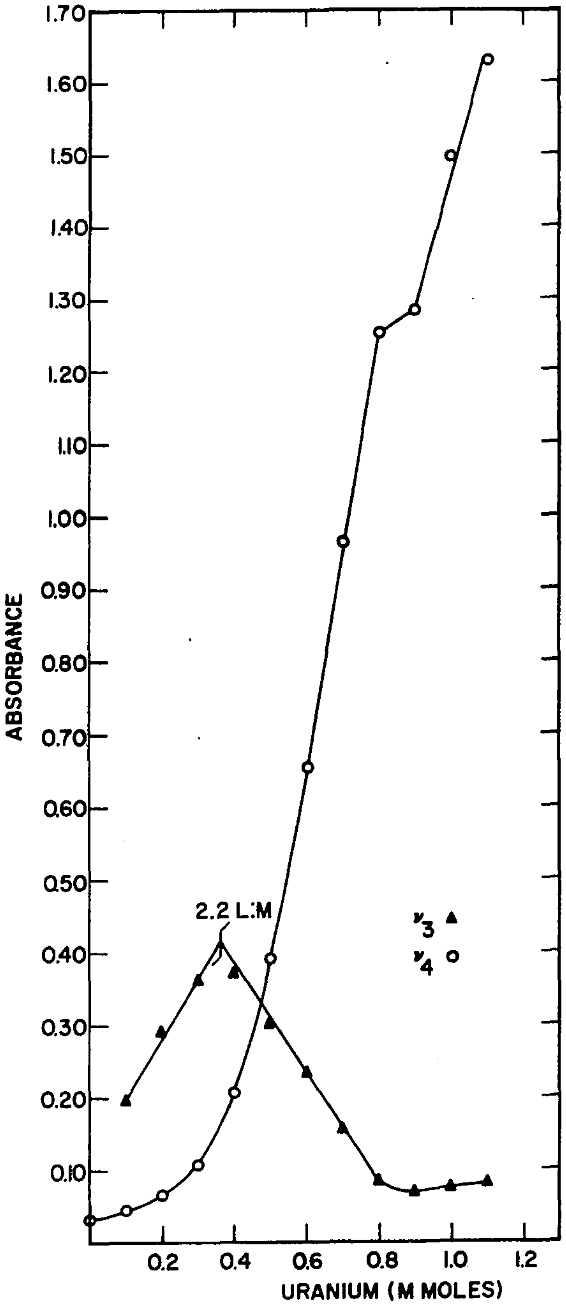
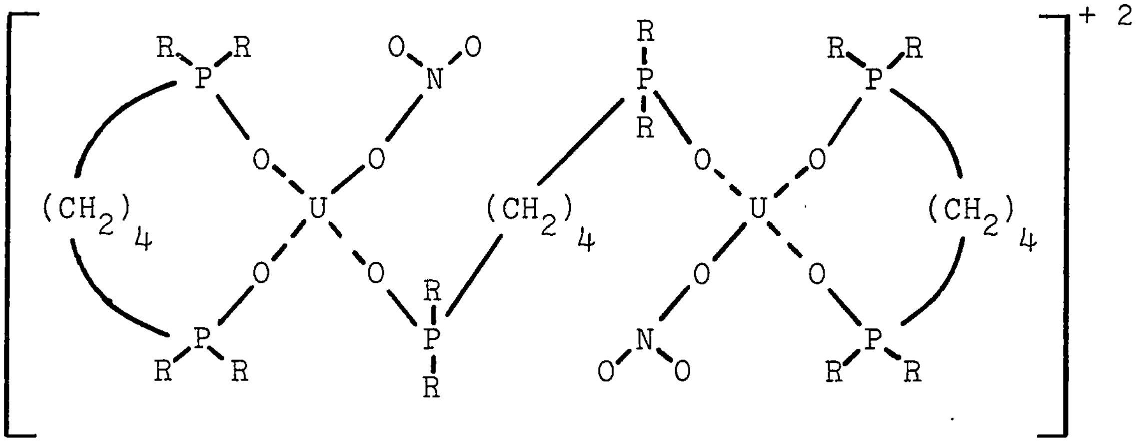


Figure 31. Covalent (ν_4) and ionic (ν_3) nitrate bands of uranium(VI) nitrate complexes of HDPE

of the ν_4 absorbance data for HDPB (Figure 35) was observed to approximately double for HDPB/U ratios between 1.33 and 1 with a concurrent decrease in the absorbance of $\nu_3(NO_3^{-1})$. This was interpreted as indicating that the higher complex had one covalent and one ionic nitrate group. The partition data (Figure 15) and the absorbance data (Figure 24) seemed to indicate the formation of a sesquisolvated bidentate complex with a possible structure being two uranium atoms bridged by a HDPB molecule with a second HDPB molecule coordinated through both phosphoryl oxygens to each uranium. One covalent nitrato group coordinated to each uranium atom would then satisfy a coordination number of four. The uranyl oxygens are not



pictured in the above structure; they would presumably lie above and below the plane of the paper with the ligands surrounding the metal atoms in a equatorial belt in the plane of

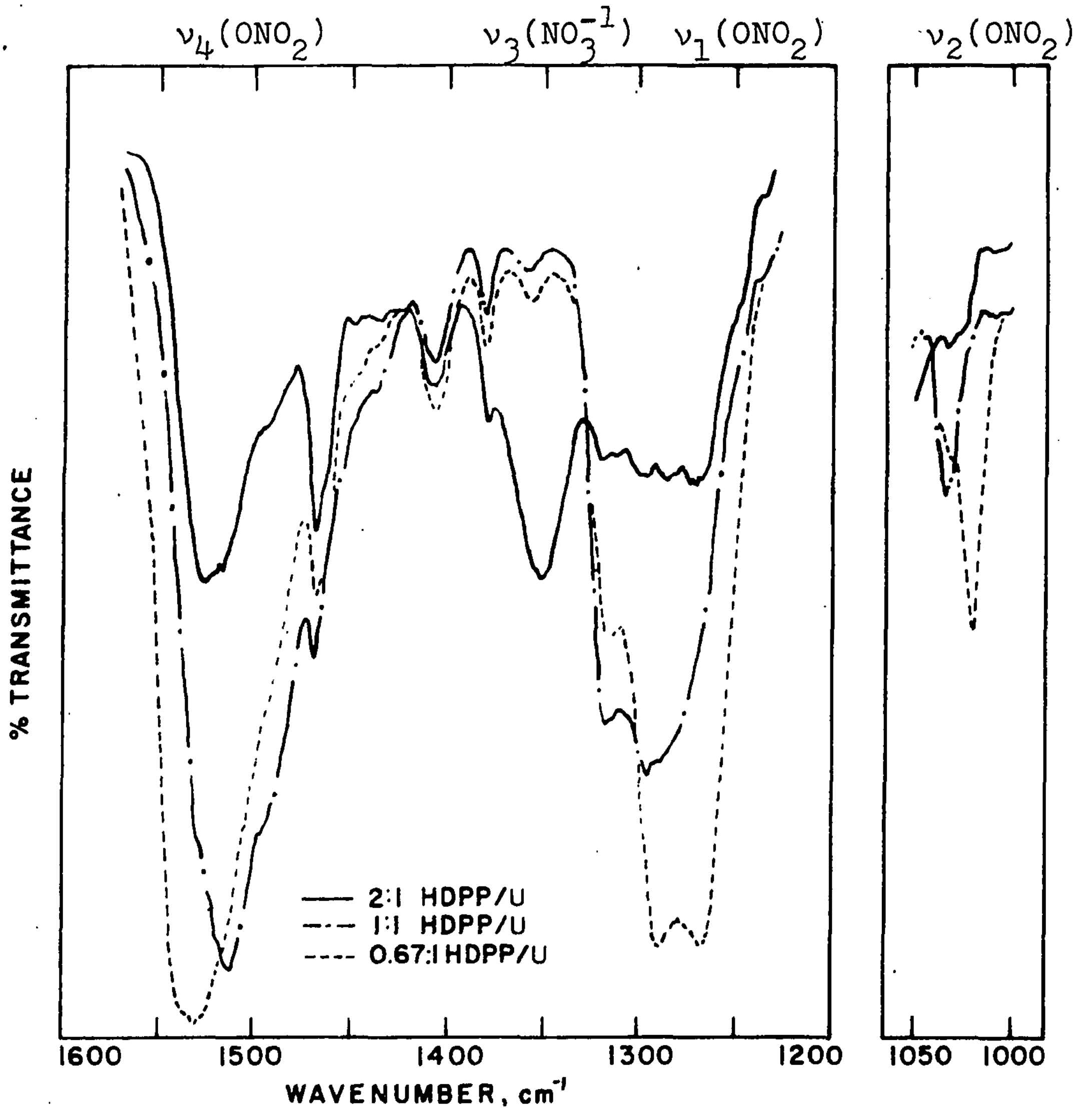
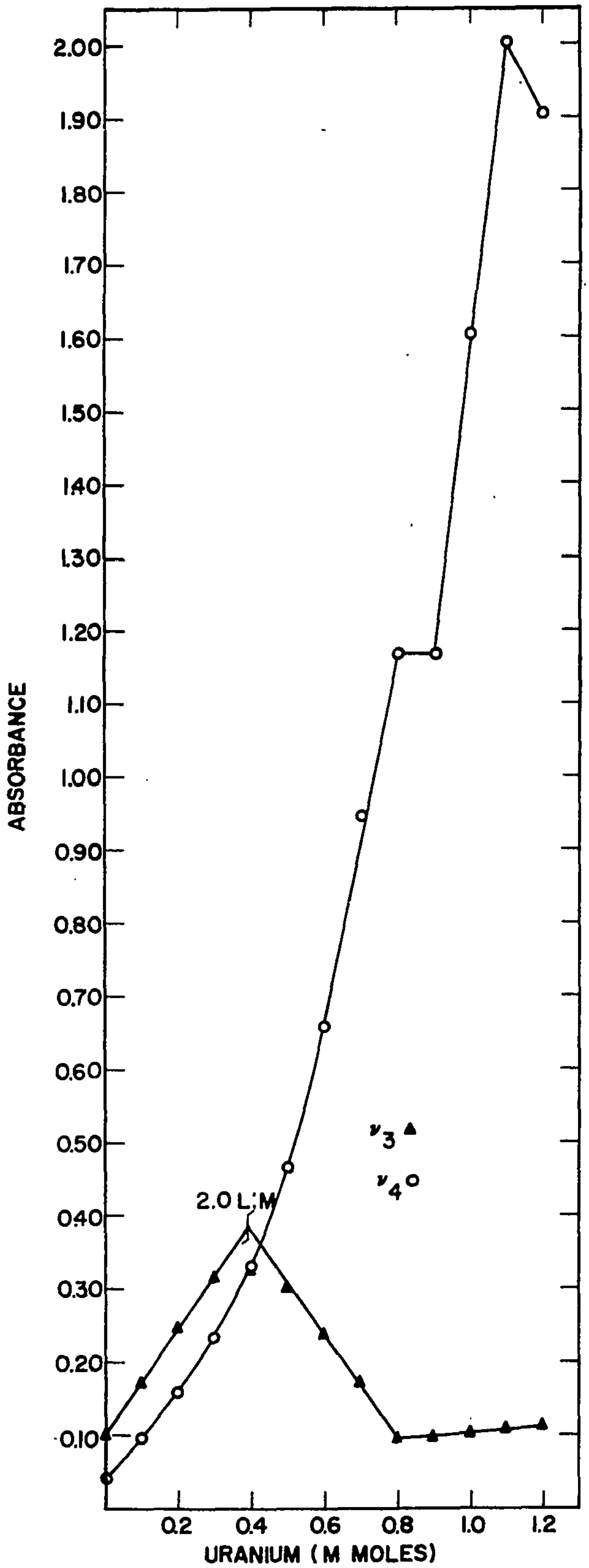


Figure 32. Spectra of covalent (ν_4, ν_1, ν_2) and ionic (ν_3) nitrate regions for uranium(VI) nitrate complexes of HDPP

Figure 33. Covalent (ν_4) and ionic (ν_3) nitrate bands of uranium(VI) nitrate complexes of HDPP


ABSORBANCE
2.00
1.90
1.80
1.70
1.60
1.50
1.40
1.30
1.20
1.10
1.00
0.90
0.80
0.70
0.60
0.50
0.40
0.30
0.20
0.10
0.2
0.4
0.6
0.8
1.0
1.2
URANIUM (M MOLES)
2.0 L:M
ν3 ▲
ν4 ○

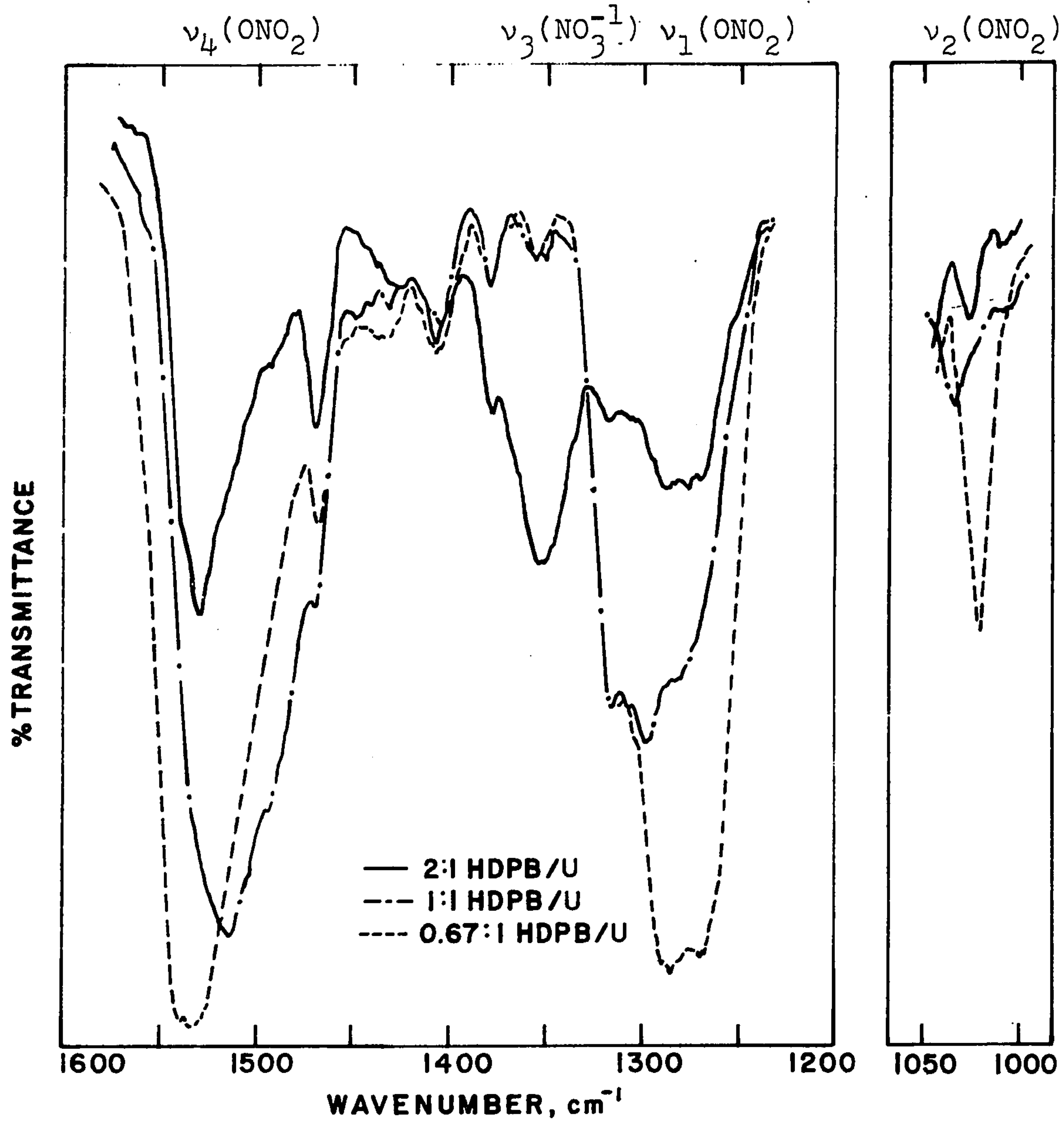


Figure 34. Spectra of covalent (ν_4, ν_1, ν_2) and ionic (ν_3) nitrate regions for uranium(VI) nitrate complexes of HDPB

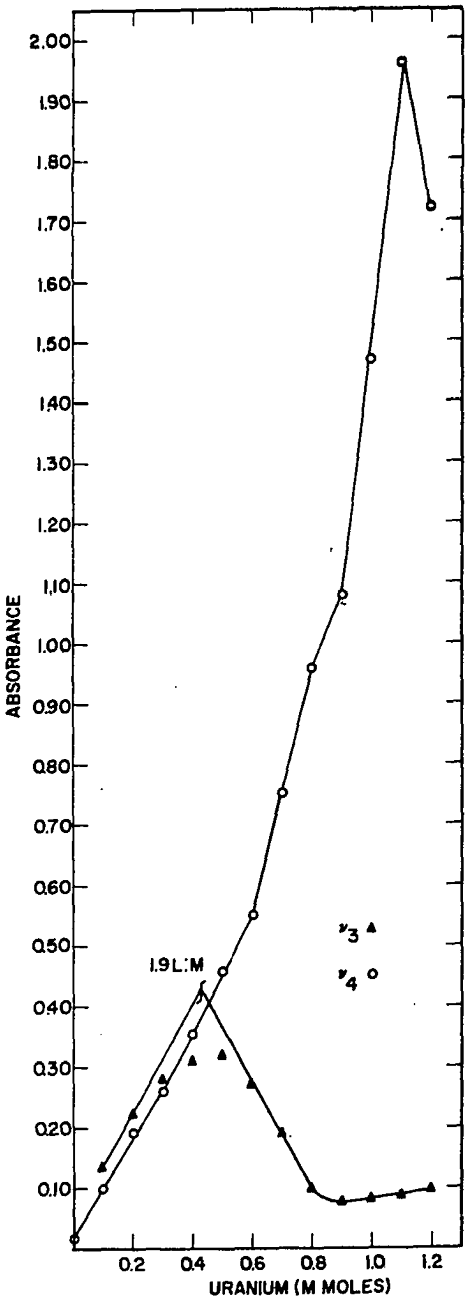


Figure 35. Covalent (ν_4) and ionic (ν_3) nitrate bands of uranium(VI) nitrate complexes of HDPB

the paper.

The absorbance data of ν_4 for HDPP (Figure 33), when plotted versus the amount of uranium present, gave a curved line in contrast to the straight line plot of the same data for HDPB. This may be indicative of mixed monosolvate and disolvate formation as suggested from the appearance of the complexed phosphoryl spectra (Figure 22). The monosolvate undoubtedly exhibits chelate ring formation but the disolvate may have the second molecule coordinated through either one or two phosphoryl oxygens. No conclusions defining the coordination of the second molecule can be drawn from these data.

The $\Delta(\nu_4 - \nu_1)$ splittings for the strongest nitrato bands were observed to decrease as the ligand/metal ratio approached one for both HDPP and HDPB (Tables 29, 30). This may be explained by decreased covalency induced by coordination of the second nitrate group which occurred upon transformation of the higher complex with one covalent and one ionic nitrate into the monosolvated chelate with two covalent nitrate groups (assuming that only one nitrate group is coordinated to uranium in the higher complex of HDPP). Stronger bonding would be required of a single covalent nitrate group as opposed to the metal-oxygen bond strength which would be required if two nitrates were coordinated because of the higher charge on the cation for the former.

Values of $\Delta(\nu_4 - \nu_1)$ for the higher complexes of HDPP and

Table 30. Frequency data for nitrato bands of $UO_2(NO_3)_2\cdot\nu HDPP$

Ratio, HDPP/U	$\nu_4(ONO_2)$	$\nu_1(ONO_2)$	$\Delta(\nu_4 - \nu_1)$	$\nu_2(ONO_2)$
8	1529 m	1318 b		1024-35 bw
4	1497 w sh 1528 s*	1308 w 1264 m*	189 264	1031 w sh 1026 w*
2.67	1495 w sh 1514 m sh 1528 s*	1308 m* -- b 1268 m*	187 -- 260	1034 w* 1026 w*
2	1495 w sh 1513 m sh 1526 s*	1314 m* 1293 m* 1268 m*	181 220 258	1033 w sh 1025 w*
1.33	1495 m sh 1514 s* sh	1316 m sh 1298 s* 1278 s sh	179 216 --	1034 m* 1026 m sh
1	1495 m sh 1514 s* sh	1317 m sh 1295 s* 1276 m sh	178 219 --	1034 m* 1024 w sh
0.80	1495 m sh -- 1533 s*	1316 m sh 1289 s* 1268 s*	179 -- 265	1034 w sh 1020 s*

w-weak, m-medium, s-strong, b-broad, sh-shoulder, w sh-weak shoulder, etc.

---

*Strongest band.

HDPB (Tables 30, 31; ligand/U-8 to 1.3) were comparable to values obtained for the hemisolvated bidentate complexes (*ibid*.; ligand/U-0.80). As the second nitrate group entered the coordination sphere, the charge on the metal cation was

Table 31. Frequency data for nitrato bands of $UO_2(NO_3)_2 \cdot \nu HDPB$

Ratio, HDPB/U	$\nu_4(ONO_2)$	$\nu_1(ONO_2)$	$\Delta(\nu_4 - \nu_1)$	$\nu_2(ONO_2)$
8	1529 m	--	--	--
		1288 sh*	--	
4	1530 s	1275 sh	255	1026 w
		1266 sh	--	
	1497 sh	--	--	
2.67	--	1290 sh	--	1026 w
	1528 s*	1273 m	255	
	1493 sh	1317 sh	176	
2	--	1287 sh*	--	1026 w
	1529 s*	1275 sh*	254	
	1493 sh	1316 m	177	
1.33	1520 s*	1286 m*	234	1031 w
	1526 s*	1273 sh	253	
	1493 sh	1315 sh	178	
1	1514 s*	1298 s*	216	1034 w
	--	1281 sh	--	
	1493 sh	1313 sh	180	
0.80	1514 sh	1290 s*	224	1034 w sh
	1533 s*	1269 s*	264	1020 s*

w-weak, m-medium, s-strong, sh-shoulder, w sh-weak shoulder

*Strongest band.

reduced and the nitrate covalency was reduced as indicated by decreased splitting values, $\Delta(\nu_4 - \nu_1)$. This might also explain the slight increase in frequency observed for the strong complexed phosphoryl band at 1085 cm^{-1} (Table 23) for HDPP if the assumption that this band was caused by the monosolvated chelate is correct. A stronger interaction and consequently a lower frequency band would be expected for the P-O entity coordinated to a uranium atom with only one covalent nitrato group. As the second nitrate group entered the coordination sphere, the charge on the metal cation would be reduced and thus interaction with the phosphoryl oxygen should be decreased resulting in a frequency shift toward higher frequencies, i.e, toward the uncomplexed phosphoryl band.

A sharply broadened (in the direction of higher frequency) complexed phosphoryl band was noted for a 1:1 HDPB/U ratio (Table 25). A similar sharp decrease in $\Delta(\nu_4 - \nu_1)$ splitting was observed at the same ligand/metal ratio (Table 31). The band at 1084 cm^{-1} was identified with a sesquisolvate and the broadening occurred in the direction of the shoulder at 1110 cm^{-1} which was identified with the monosolvated chelate (Figure 24). No reasonable explanation can be advanced for these observations.

Additional confirmatory evidence for a decrease in the interaction of the nitrato group with uranium as the ligand/uranium ratio approached a value of one was obtained by observing intensity changes of the $\nu_2(ONO_2)$ bands of HDPP and HDPB (Tables 30, 31). These data indicated that, initially, the most intense band was the lower frequency band (1024-26 cm^{-1}) but as the ratio approached one the higher frequency band (1033-34 cm^{-1}) became the most intense while the low frequency band only appeared as a weak shoulder. This trend was immediately reversed when the ligand/metal ratio was decreased below one; the low frequency band was strongly intensified whereas the high frequency band showed a considerable decrease in intensity (Figure 30, 32) and concurrently, a increase in $\Delta(\nu_4 - \nu_1)$ was observed (Tables 30, 31). These data again seemed to confirm formation of a hemisolvated bidentate complex. This species appeared to be present in larger concentration for HDPP and HDPB (loading capacity for both compounds was 0.68 ligand/metal) than for HDPM (0.84 ligand/metal) and HDPE (0.75 ligand/metal) (Table 18). This was not unexpected because greater separation between the phosphoryl groups of the ligand should allow each group to more easily coordinate independantly because of decreased steric interaction.

The nitrate spectra for TOPO (Figure 34) were interpreted in substantially the same manner as for the four bidentate organophosphorus compounds. Several basic differences were noted, as expected, since TOPO behaves somewhat differently because it is a monodentate ligand. The degree of covalency of the nitrato groups, as measured by $\Delta(\nu_4 - \nu_1)$, was observed to increase substantially as the TOPO/U ratio was decreased below two (Table 32). This was anticipated since it was shown previously that the disolvate appeared to be the species present in the greatest concentration and monosolvate formation was indicated by a loading capacity of 1.11 TOPO/U (Table 18).

Partition (Figure 14) and absorbance (Figure 17) data suggested that a trisolvated complex, $UO_2(NO_3)_2 \cdot 3TOPO$, present in relatively low concentration, appeared to be formed in the presence of excess ligand. It was expected that trisolvate formation should result in the displacement of one of the covalent nitrate groups from the coordination sphere, again assuming a coordination number of four for uranium. Confirming this expectation, a relatively small band was observed to initially increase in intensity in the ionic nitrate region (1350 cm^{-1}) and then decrease (ν_3, Figure 37). The absorbance of the covalent nitrato band (ν_4) increased quite rapidly as shown by the initial slope of the curve in Figure 37 thus indicating a rapid increase in the amount of this entity. An increased number of bands in the asymmetric stretching region of the covalent nitrato band, $\nu_4(ONO_2)$, were noted for TOPO-uranium mixtures (Table 32). An explanation of the number of bands can not be given although the possibility of bidentate coordination of the nitrate group should be mentioned. Cotton[1] has stated that monodentate and bidentate coordination of the

---

[1] Cotton, F. A. Cambridge, Massachusetts. Distinguishing monodentate and bidentate nitrate coordination by infrared spectroscopy. Private communication. May, 1963.

nitrate group could not be distinguished from infrared spectral data.

The main nitrato bands (marked with an asterisk) remained at a relatively constant frequency (Table 32) until the TOPO/U ratio was decreased below two in contrast to the frequency data observed for HDPP and HDPB (Tables 30, 31). This was as expected because the disolvate with both nitrates covalently bonded was the determining factor as it was the species present in the largest concentration.

Conductivity and Viscosity Studies

Molar conductivities based on uranium concentration were determined for various ligand/uranium ratios for HDPM, HDPE, HDPP, HDPB and TOPO in nitrobenzene solution. Minimum conductivity readings were observed at 1:1 ligand/metal ratios for the bidentate organophosphorus compounds and a 2:1 ratio for TOPO (Figure 38). These minima corresponded to the formation of highly covalent monosolvated complexes for the bidentate ligands and a disolvated complex for TOPO.

Viscosity data for HDPM and HDPB were indicative of discrete complex formation rather than formation of polymeric species since viscosities decreased with decreasing ligand/metal ratios (Table 33).

These data appeared to confirm chelate ring formation for the monosolvated uranium(VI) nitrate complexes of the bidentate

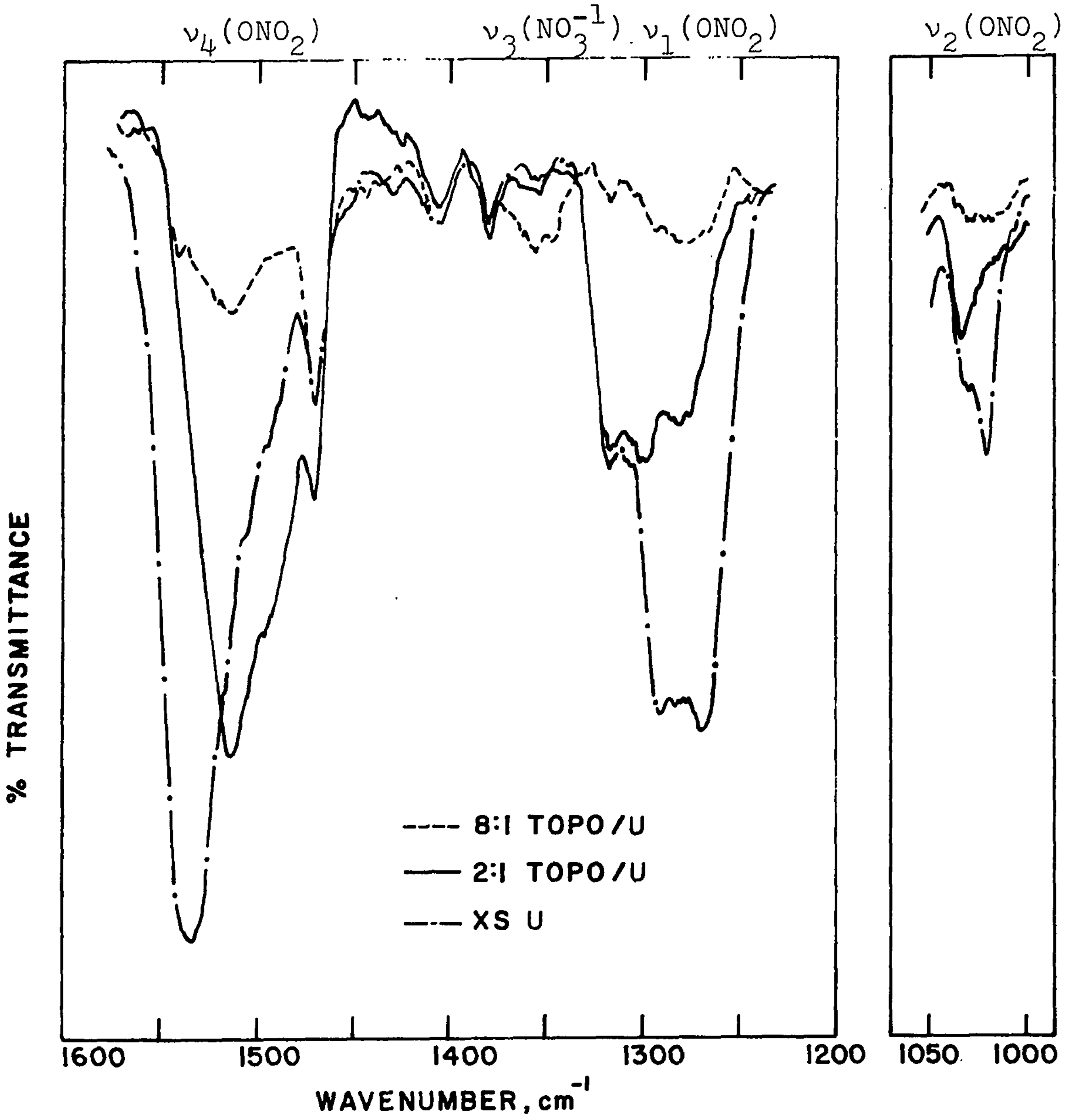


Figure 36. Spectra of covalent (ν_4, ν_1, ν_2) and ionic (ν_3) nitrate regions for uranium(VI) nitrate complexes of TOPO

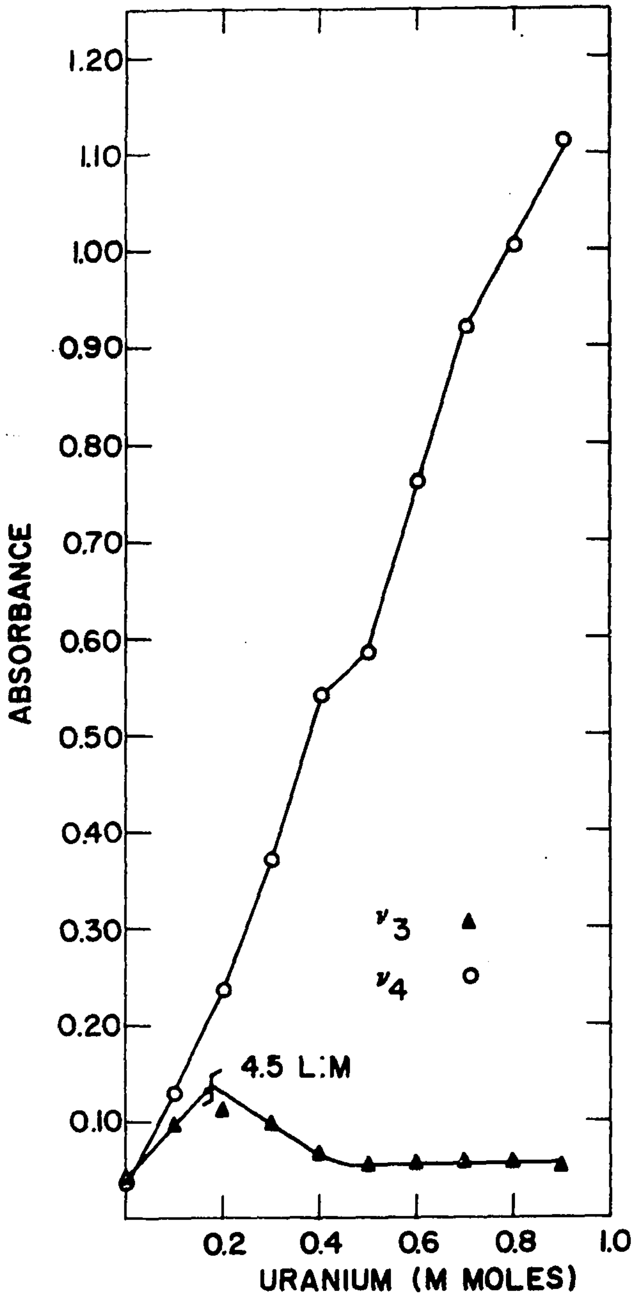


Figure 37. Covalent (ν_4) and ionic (ν_3) nitrate bands of uranium(VI) nitrate complexes of TOPO

Table 32. Frequency data for nitrato bands of $UO_2(NO_3)_2 \cdot TOPO$

Ratio, TOPO/U	$\nu_4(ONO_2)$	$\nu_1(ONO_2)$	$\Delta(\nu_4 - \nu_1)$	$\nu_2(ONO_2)$
8	1514 s*	1318 w	--	b
	1520 sh	--	--	
	1541 sh	1279 b*	--	
4	1487 sh 1522 sh	1316 sh	--	1033 w
	1505 sh 1534 sh	1296 sh*	--	
	1515 s* 1540 sh	1277 sh	--	
2.67	1491 sh 1520 sh	1318 sh	--	1033 w
	1505 sh	1294 m*	--	
	1514 s* 1540 sh	1276 sh	--	
2	1496 sh	1318 m	178	1033 w
	--	1300 m*	--	
	1513 s*	1281 sh	232	
1.6	1493 sh	1318 w sh	175	1032 w sh
	1521 sh	1291 s*	230	1021 m*
	1532 s*	1272 s*	260	
1.33	1496 sh	1313 w sh	183	1029 w sh
	--	1290 s*	--	1021 m*
	1533 s*	1274 s*	259	

w-weak, m-medium, s-strong, b-broad, sh-shoulder, w sh-weak shoulder

---

*Strongest band.

organophosphorus compounds.

Ionization was indicated by the increases in molar conductivity as the ligand/uranium ratio was increased (Figure 38). The molar conductivities at infinite dilution (Table 34)

Figure 38. Molar conductance data for uranium(VI) nitrate-organophosphorus reagent mixtures as a function of ligand/uranium ratio (constant uranium(VI) nitrate concentration) diluent-nitrobenzene

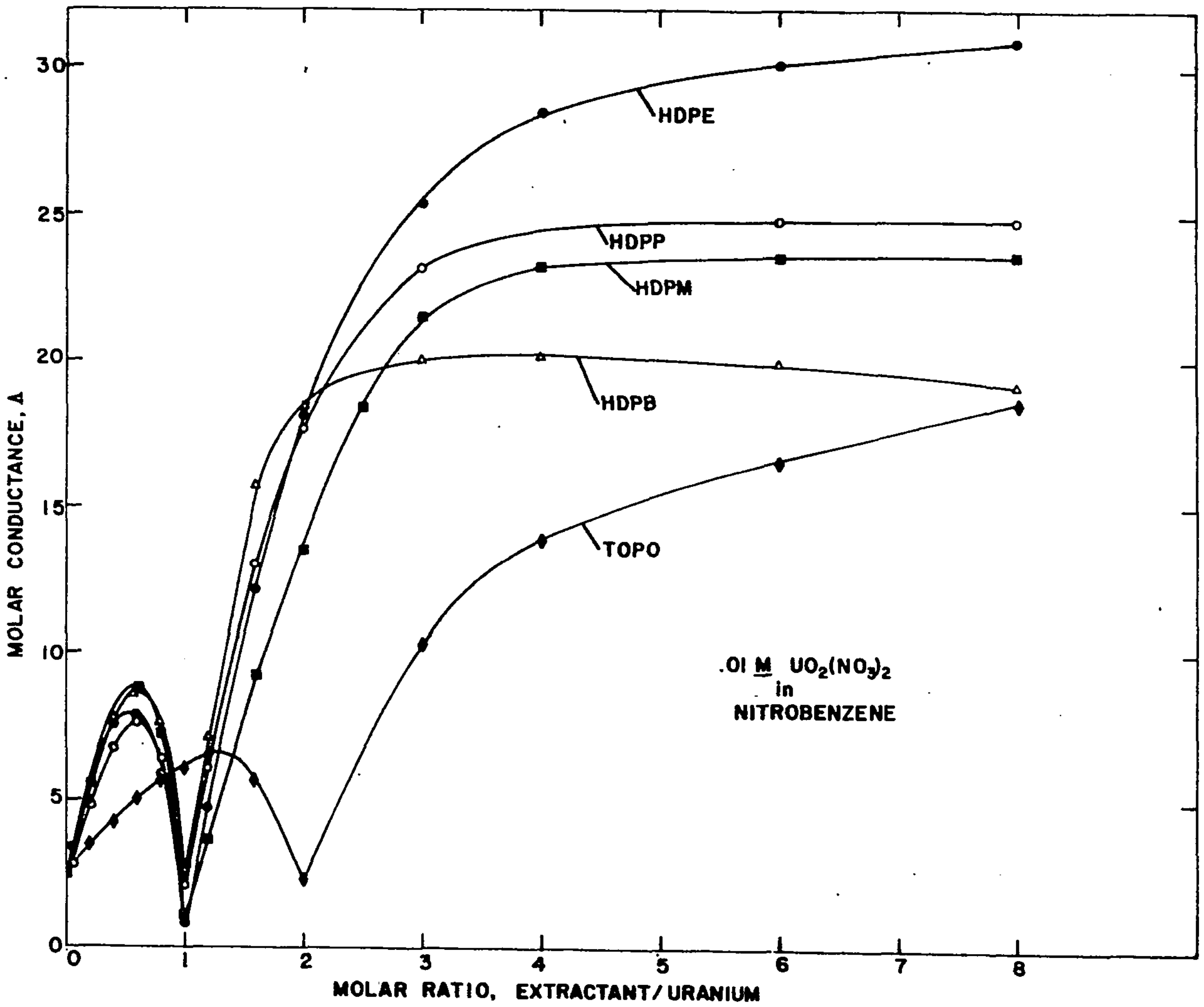

MOLAR CONDUCTANCE, Λ
0
5
10
15
20
25
30
MOLAR RATIO, EXTRACTANT/URANIUM
0
1
2
3
4
5
6
7
8
HDPE
HDPP
HDPM
HDPB
TOPO
.01 M $UO_2(NO_3)_2$
in
NITROBENZENE

Table 33. Variation of viscosity with ligand/uranium[a] ratio for HDPM and HDPB

Ligand/uranium ratio	(centipoises) 25° C HDPM	HDPB
8	1.987	2.026
6	1.956	1.976
4	1.943	1.940
3	1.891	1.899
2.5	1.879	
2		1.870
1.6	1.843	1.851
1.2	1.834	1.841
1	1.823	1.829
0.8	1.829	1.824
0.4	1.805	1.809
0.2	1.809	1.810
0.04	1.813	1.816

diluent-nitrobenzene

[a] Uranium(VI) nitrate concentration maintained constant at 0.01 M

Table 34. Molar conductivity at infinite dilution for uranium (VI) nitrate complexes of HDPM, HDPE, HDPP and HDPB

Compound	Λ_o - 25° C
HDPM	50
HDPE	43
HDPP	32
HDPB	30

were obtained by determining the conductivity of successive dilutions of the solutions containing a 6:1 ligand/metal ratio, plotting these data against the square root of the concentration of uranium and extrapolation to zero concentration. These data indicated increased ionization for HDPM and HDPE in agreement with 2:1 electrolyte formation as postulated from the infrared data.

No sound theoretical explanation can be advanced for the conductance maxima observed at approximately a 0.6 ligand/metal ratio for the bidentate ligands and similarily at a 1:2 ligand/metal ratio for TOPO. One may postulate several possible explanations of the phenomena though. The appearance of maxima and their location with respect to the abscissa for all the ligands suggested that they were connected with the formation of complexes solvated with one P-O group. A tentative explanation might be a partial ionization of a nitrate group caused by the initial coordination of a P-O group to the uranium atom causing a small increase in molar conductance followed by loss of coordinated water which in turn resulted in increased covalency of the anions causing a decrease in conductance. Another possible explanation may be the transformation of hexacoordinated uranium(VI) into tetracoordinated uranium(VI). The former species might be expected to exhibit a lower mobility than the latter thus leading to the observed maxima.

Visible Spectral Studies

The spectra of some of the 1,2-dichloroethane solutions (from infrared study) containing varying ratios of organophosphorus compound/uranium(VI) nitrate were scanned over the visible region (320-500 mμ) (Figure 39, 40, 41, 42, 43). All spectra of solutions with the same ligand/metal ratio are comparable since the same concentrations of ligand and uranium were used throughout. The spectra of 0.1 M solutions of HDPM, HDPE and HDPB in 1,2-dichloroethane equilibrated with 0.025 M aqueous uranium(VI) perchlorate were also obtained (Figure 44). All spectra were displaced upward in a nonuniform manner so as to give the best overall picture while maintaining the vertical height of the figures within reasonable bounds. No significant spectral changes were noted for the solutions which were dried with molecular sieves (Linde, 4A) and thus all spectra are of solutions containing varying amounts of water introduced by the dihydrated uranium salt used in these studies.

The visible spectra of uranium-HDPM mixtures exhibited well-resolved fine structure for HDPM/U ratios ≥ 2 (curves a, b and c, Figure 39) with 14 bands visible in the region, 340-500 mμ. Resolution was decreased in the 470-500 mμ region when the HDPM/U ratio was decreased below two (curve d, Figure 39). A decrease in resolution in this same region was also noted for HDPE (curve d, Figure 40).

A noticeable splitting of the most intense band occurred for HDPM, HDPE and HDPB when the ligand/metal ratio was decreased below two (Figure 39, 40, 41). The intensity of this second band, located at approximately 420 mμ, increased until the ligand/metal ratio reached one and then remained constant while the 425 mμ band increased again. Closely spaced doublets were observed in the spectra of HDPB-uranium solutions for high ligand/metal ratios (curves a, b and c, Figure 42).

The spectra of all five organophosphorus compounds exhibited a band at 488 mμ for a 1:1 ligand/metal (2:1 for TOPO) ratio (curve e, Figure 39, 40, 41, 42; curve c, Figure 43). This band was not observed in the spectra of solutions which contained higher ligand/metal ratios. This band may be additional evidence in favor of similar monosolvated chelate structures for the bidentate ligands with two coordinated nitrate groups completing the structural picture. The structure for TOPO would be the same except for the absence of a chelate ring.

Strong, sharp band structure appeared in the spectra of HDPE, HDPP and HDPB when the ligand/metal ratio was reduced below one (curve f, Figure 40, 41, 42). This same band structure appeared when the ratio was decreased below two for HDPM (curves d and e, Figure 39) and TOPO (curve d, Figure 43). This was assumed to be caused by the stronger influence of the coordinated nitrate groups on the spectra of the uranyl(VI) ion as the influence of the organophosphorus ligands decreased with decreasing ligand/metal ratios.

The similarity between the uranium(VI) perchlorate complexes of HDPM and HDPE and the difference between them and the complex of HDPB are readily seen by comparing their spectra (Figure 44). The increased fine structure observed in the electronic absorption spectra of the uranyl(VI) ion in the presence of excess HDPM or HDPE may be due to the absence of anion and/or water molecules from the coordination sphere of the metal ion. The absence of anionic influence on the electronic energy levels of uranium is suggested by comparing the spectra of the uranium(VI) nitrate and the uranium(VI) perchlorate complexes of HDPM (compare curve a or b, Figure 39 with Figure 44). This is regarded as evidence in favor of the complete displacement of the anions from the coordination sphere of uranium for both of these complexes (disolvates). The virtually identical spectra obtained for uranium(VI) perchlorate in the presence of excess HDPM or HDPE (Figure 44) is regarded as additional evidence favoring the coordination of four phosphoryl groups to uranium in the disolvated complex, $UO_2(ClO_4)_2 \cdot 2HDPE$. The absence of well-resolved fine structure from the spectra of uranium(VI) nitrate-HDPE mixtures (Figure 40) is somewhat puzzling. The anion may be exerting some influence here although the infrared spectra indicated that both nitrate groups were displaced in the presence of excess HDPE. Another possible explanation might be the presence of mixtures of complexes as this would lead to decreased fine structure.

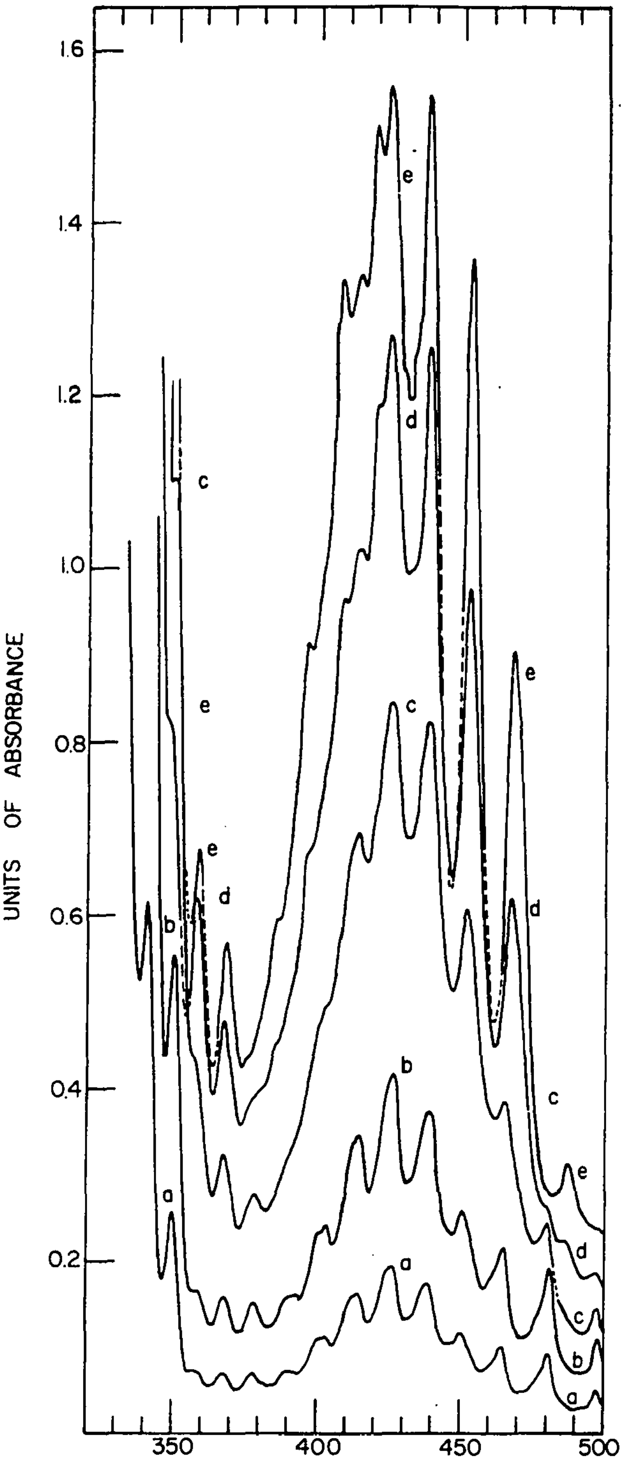


Figure 39. Changes in the visible spectrum of uranium (VI) nitrate induced by varying HDPM/U ratios of (a) 8:1, (b) 4:1, (c) 2:1, (d) 1.3:1, (e) 1:1

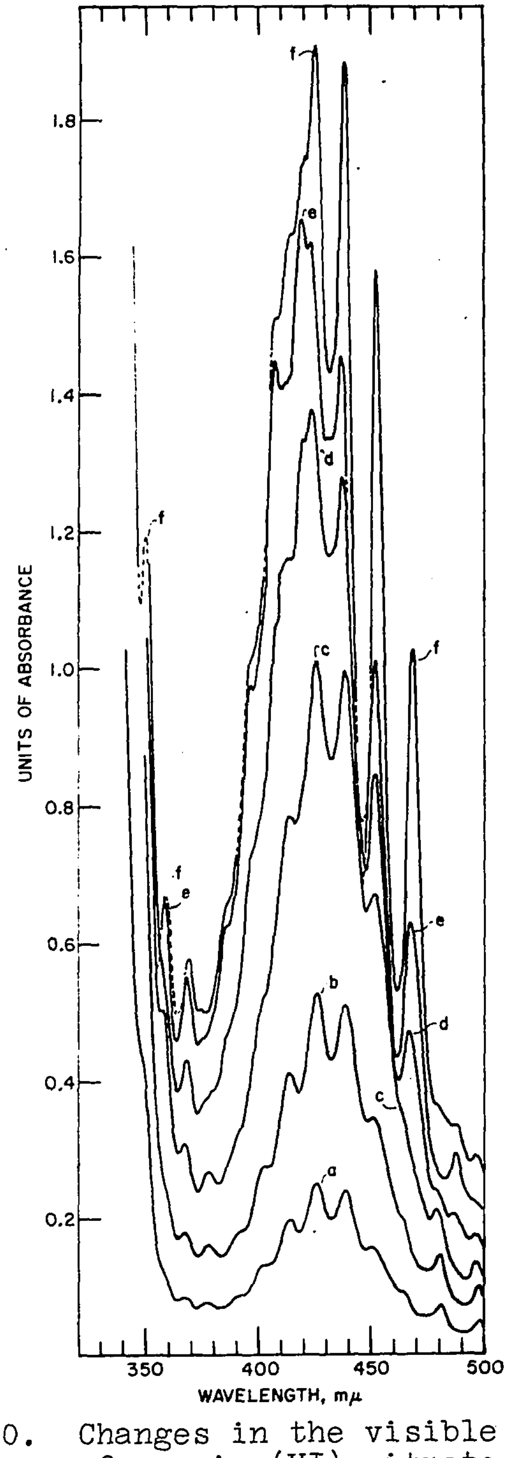


Figure 40. Changes in the visible spectrum of uranium(VI) nitrate induced by varying HDPE/U ratios of (a) 8:1, (b) 4:1, (c) 2:1, (d) 1.3:1, (e) 1:1, (f) 0.8:1

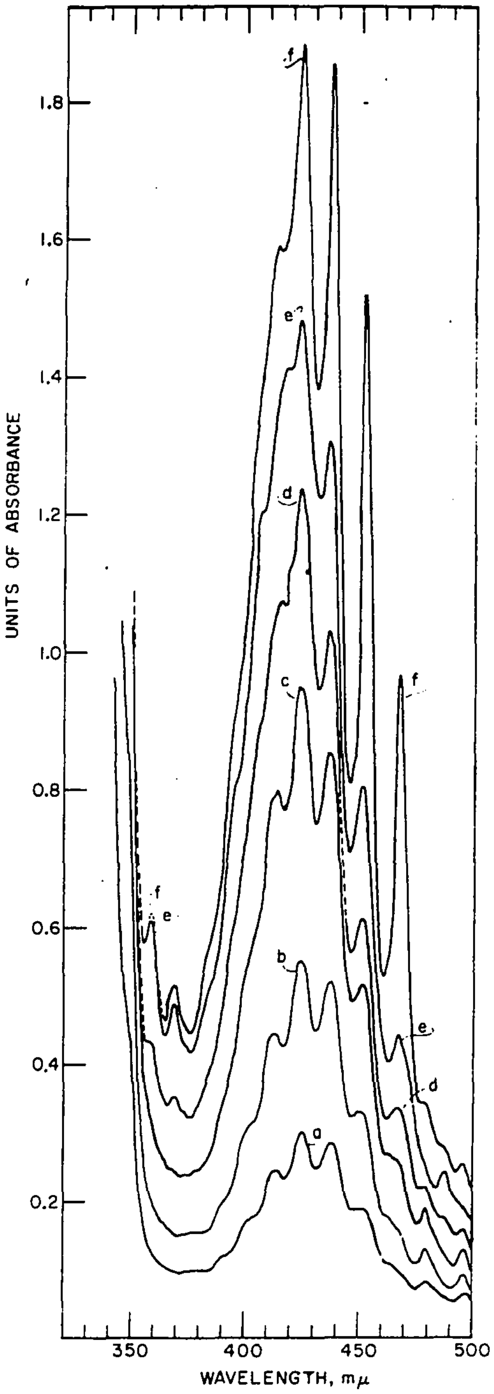


Figure 41. Changes in the visible spectrum of uranium(VI) nitrate induced by varying HDPP/U ratios of (a) 8:1, (b) 4:1, (c) 2:1, (d) 1.3:1, (e) 1:1, (f) 0.8:1

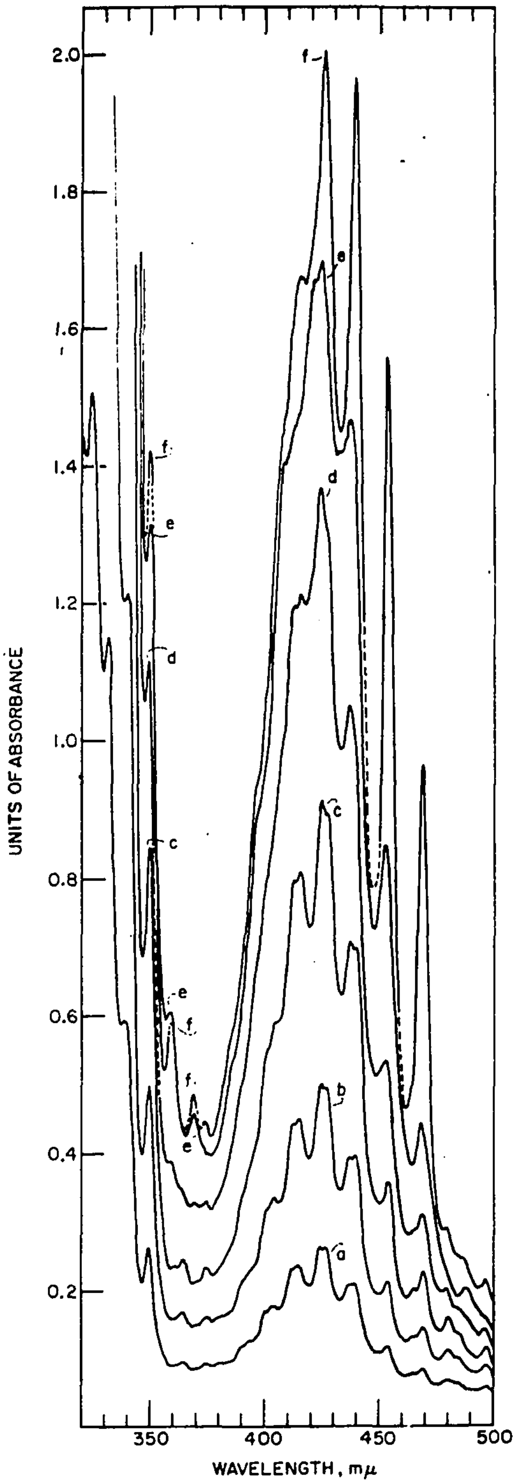


Figure 42. Changes in the visible spectrum of uranium(VI) nitrate induced by varying HDPB/U ratios of (a) 8:1, (b) 4:1, (c) 2:1, (d) 1.3:1, (e) 1:1, (f) 0.8:1

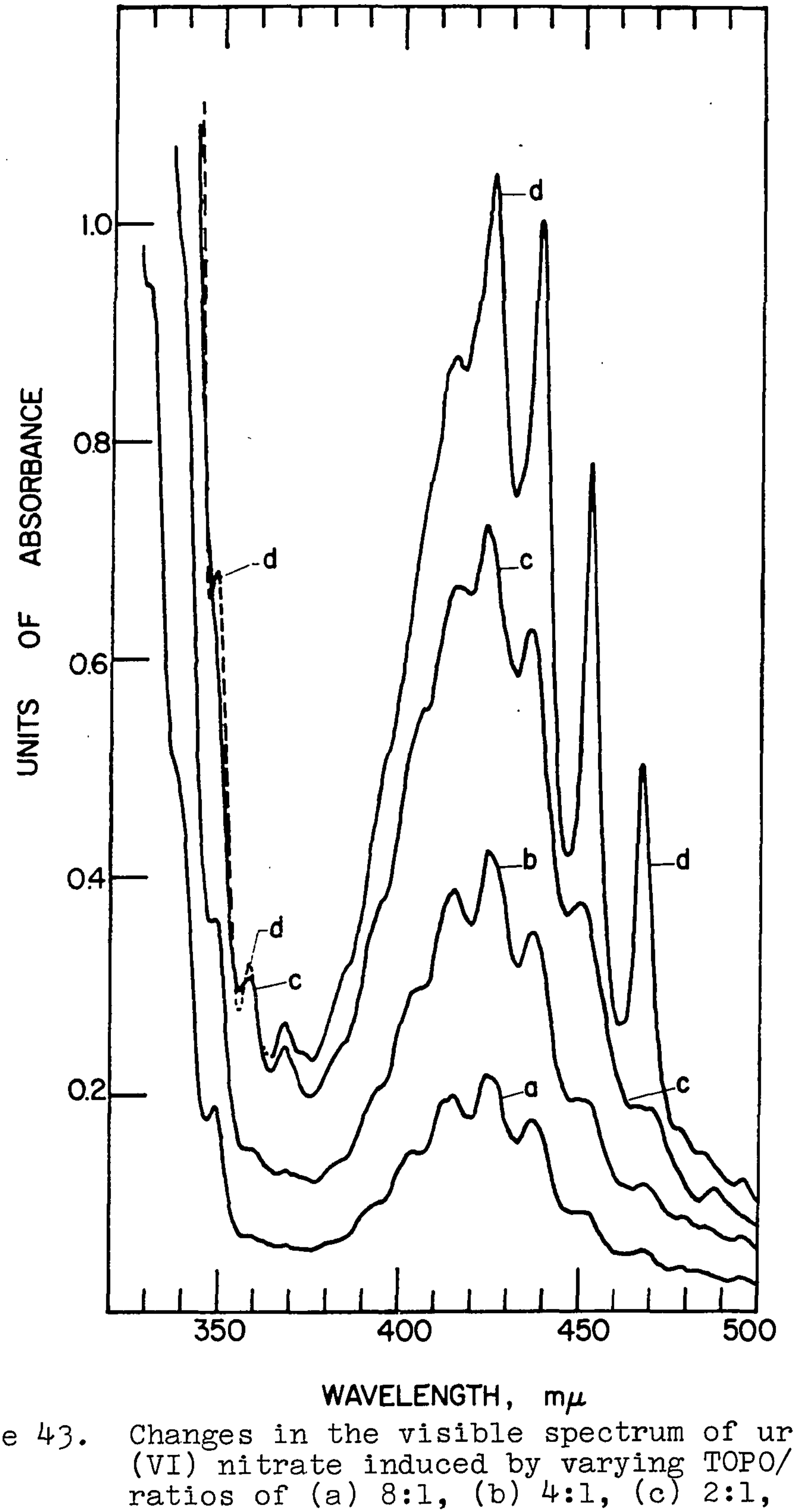


Figure 43. Changes in the visible spectrum of uranium (VI) nitrate induced by varying TOPO/U ratios of (a) 8:1, (b) 4:1, (c) 2:1, (d) 1.3:1

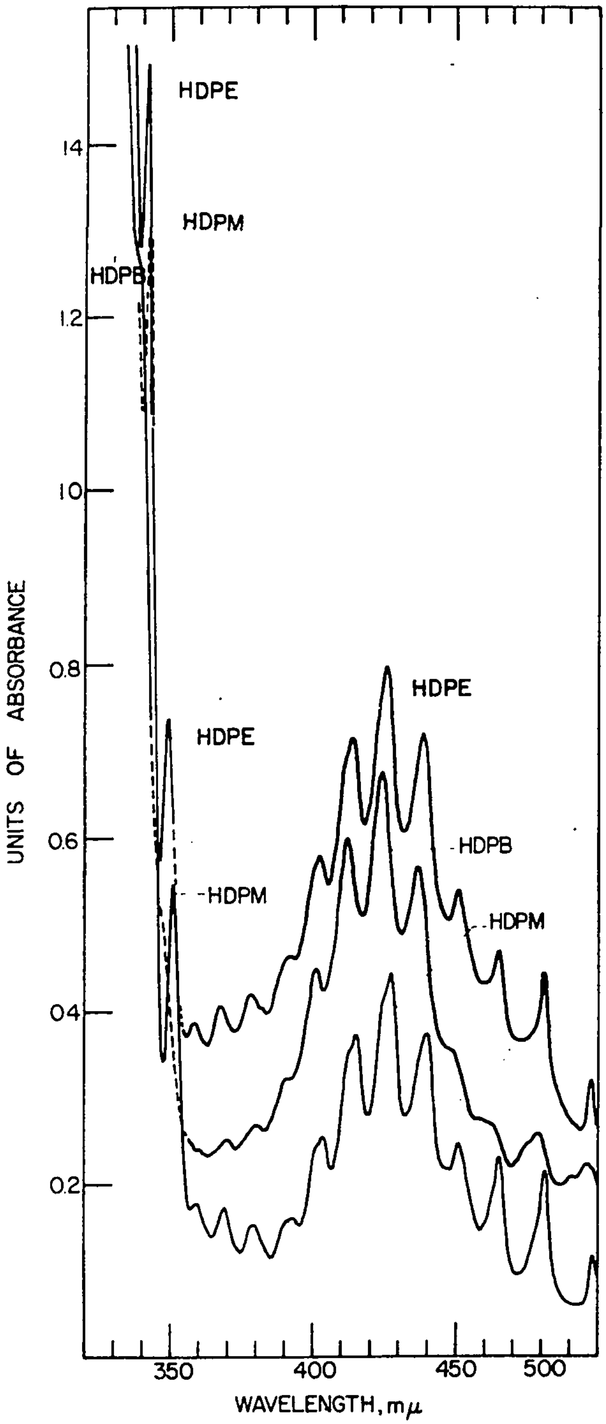


Figure 44. Spectra of uranium(VI) perchlorate complexes of HDPM, HDPE and HDPB (4:1 ligand/metal ratio)

Hydrate Formation for HDPM, HDPE, HDPP, HDPB and TOPO

Formation of a monohydrated TBP molecule has been reported by several workers with infrared, NMR and solubility data utilized to prove the existence of this species (3, 17, 72). Recently, Axtmann (5) has summarized some of the data and concluded that the weight of evidence was in favor of formation of a TBP·H_2O complex.

Nuclear magnetic resonance data

Most studies involving hydrate formation have been conducted using 100% TBP and it has been reported that the use of a inert diluent caused the solubility of water in TBP to be substantially reduced below that corresponding to a 1:1 molar ratio (52, 80). During the course of this investigation, a NMR spectrum of water-saturated, 0.15 M TBP in carbon tetrachloride was obtained. No significant formation of a hydrated species was observed at this concentration level.

The NMR spectrum of an anhydrous, 0.15 M solution of HDPM in carbon tetrachloride is shown in Figure 45. The triplet observed at 0.90 ppm was caused by the spin-coupling of protons of the terminal methyl groups of the alkyl chains to the adjacent methylene protons. The unresolved, strong band located at 1.38 ppm was due to the coupling of adjacent methylene protons while the shoulder on this band at 1.63 ppm was caused by the spin-coupling of methylene protons to the adjacent P^{31} nucleus. The downfield shift of these protons was due to their deshielding by the electronegative phosphoryl group. The triplet with a 1:2:1 area ratio, centered at 2.03 ppm, represented the unique protons of the methylene bridge coupled to the adjacent P^{31} nuclei with a coupling constant, J = 13.0 cps. The spectrum of a water-saturated, 0.15 M solution of HDPM is shown in Figure 46. Two additional bands were observed, one at 2.88 ppm and a band which merged with the center band of the triplet at 2.08 ppm. When the water content of the organic phase was decreased somewhat, two bands were resolved at 2.07 and 2.03 ppm with the former being the hydroxyl protons of water. The NMR spectrum of a partially dehydrated sample of HDPM, dried at 50-60° C (0.1 mm Hg) for seven hours, illustrated the tenacity with which the water is held (Figure 47). The band due to the hydroxyl protons of water has been shifted toward higher field (2.67 ppm) and has been reduced in intensity. There was no evidence of the second band.

The occurrence of two bands for the hydroxyl protons of water in the NMR spectrum of water-saturated solutions of HDPM was significant because it indicated the presence of water molecules in two different environments. The hydrogen bond formed with HDPM was of sufficient strength to prevent rapid proton exchange between these two environments and the subsequent appearance of a single band.

Monohydrate formation was indicated by comparison of the peak areas of the band due to the protons of the hydrogen bonded water molecule (2.88 ppm, Figure 46) and the first band of the triplet which is equivalent to 0.5 proton. The special

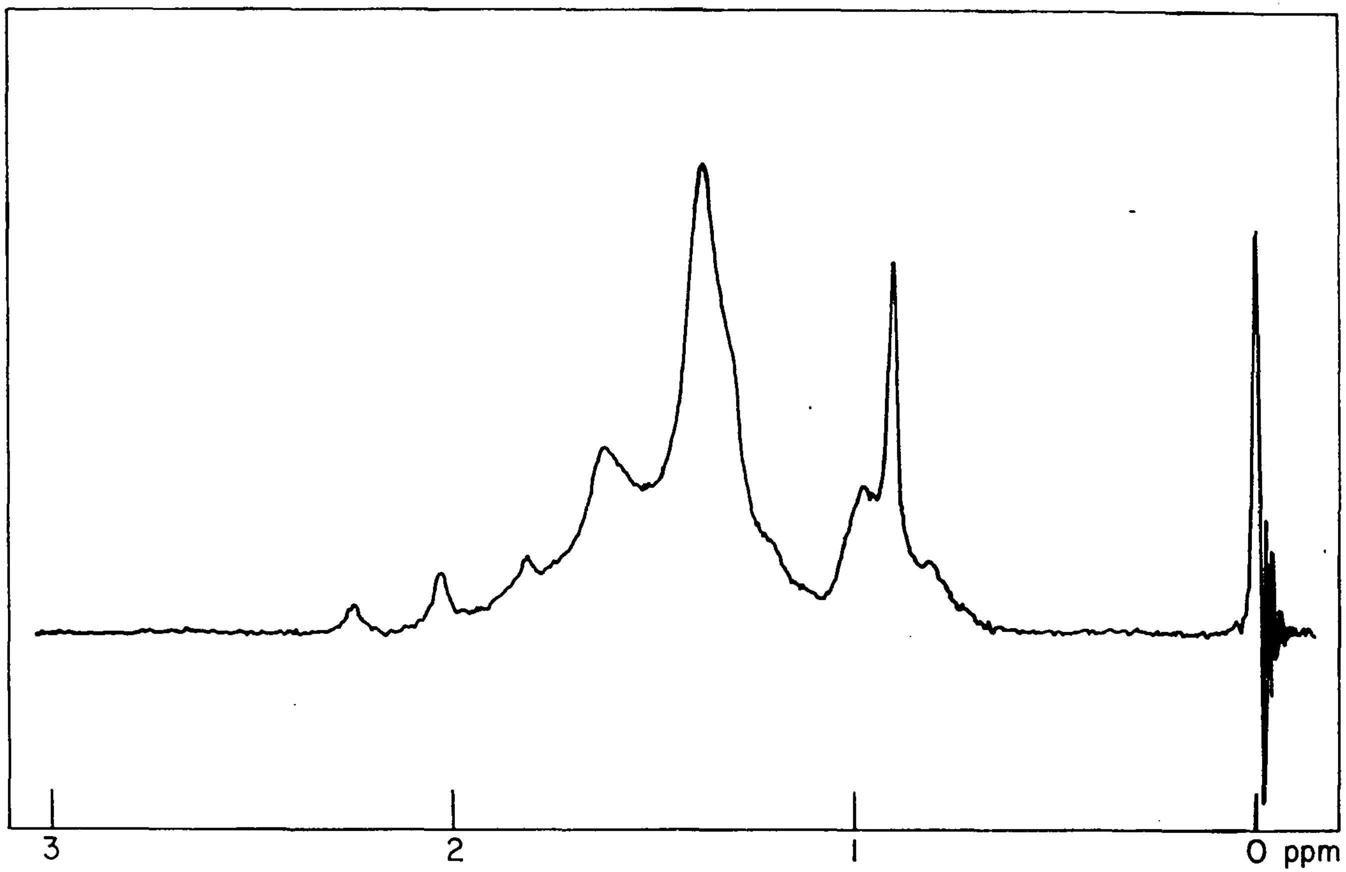


Figure 45. Nuclear magnetic resonance proton spectrum of anhydrous HDPM in carbon tetrachloride

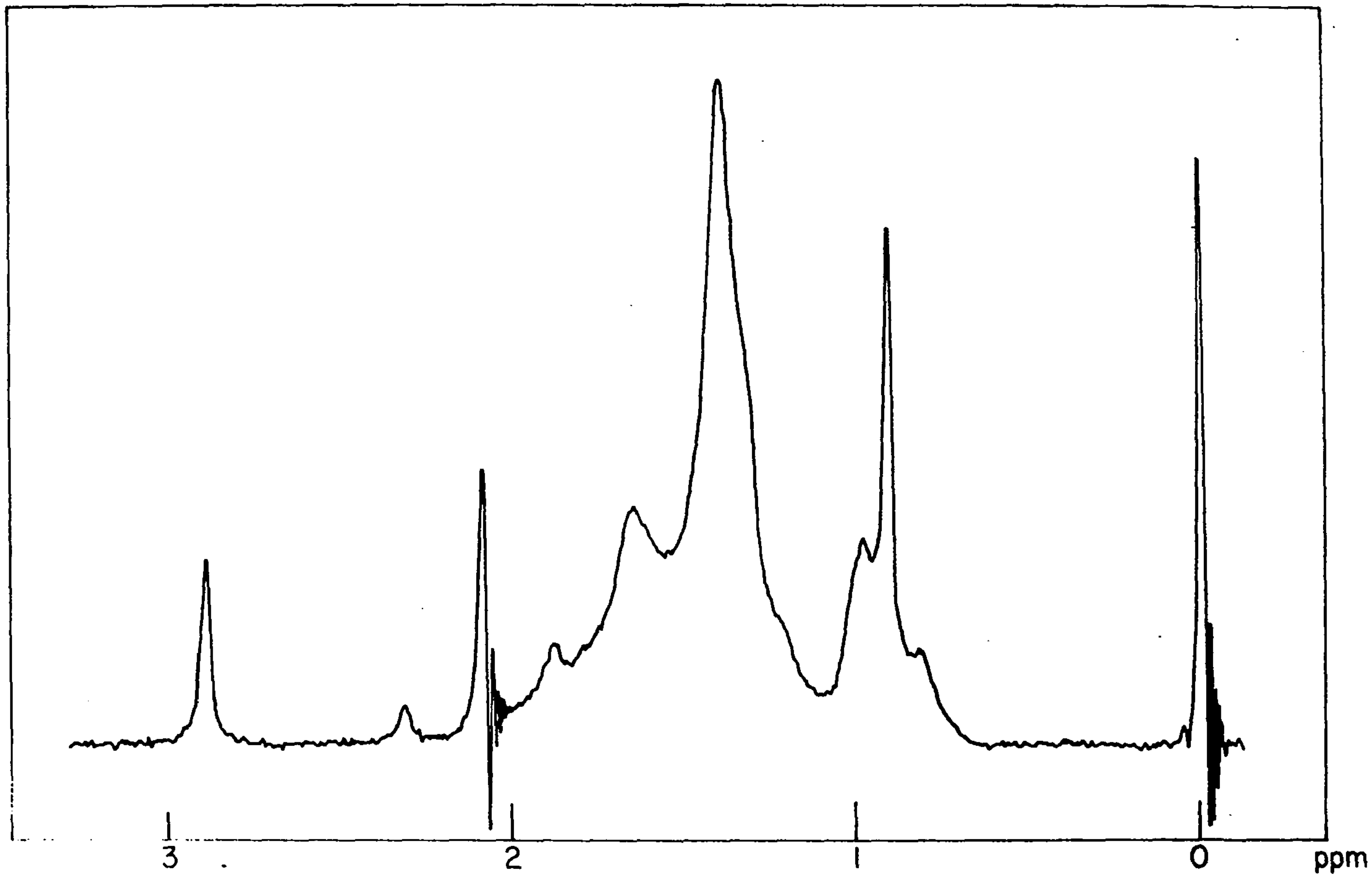


Figure 46. Nuclear magnetic resonance proton spectrum of water-saturated HDPM in carbon tetrachloride

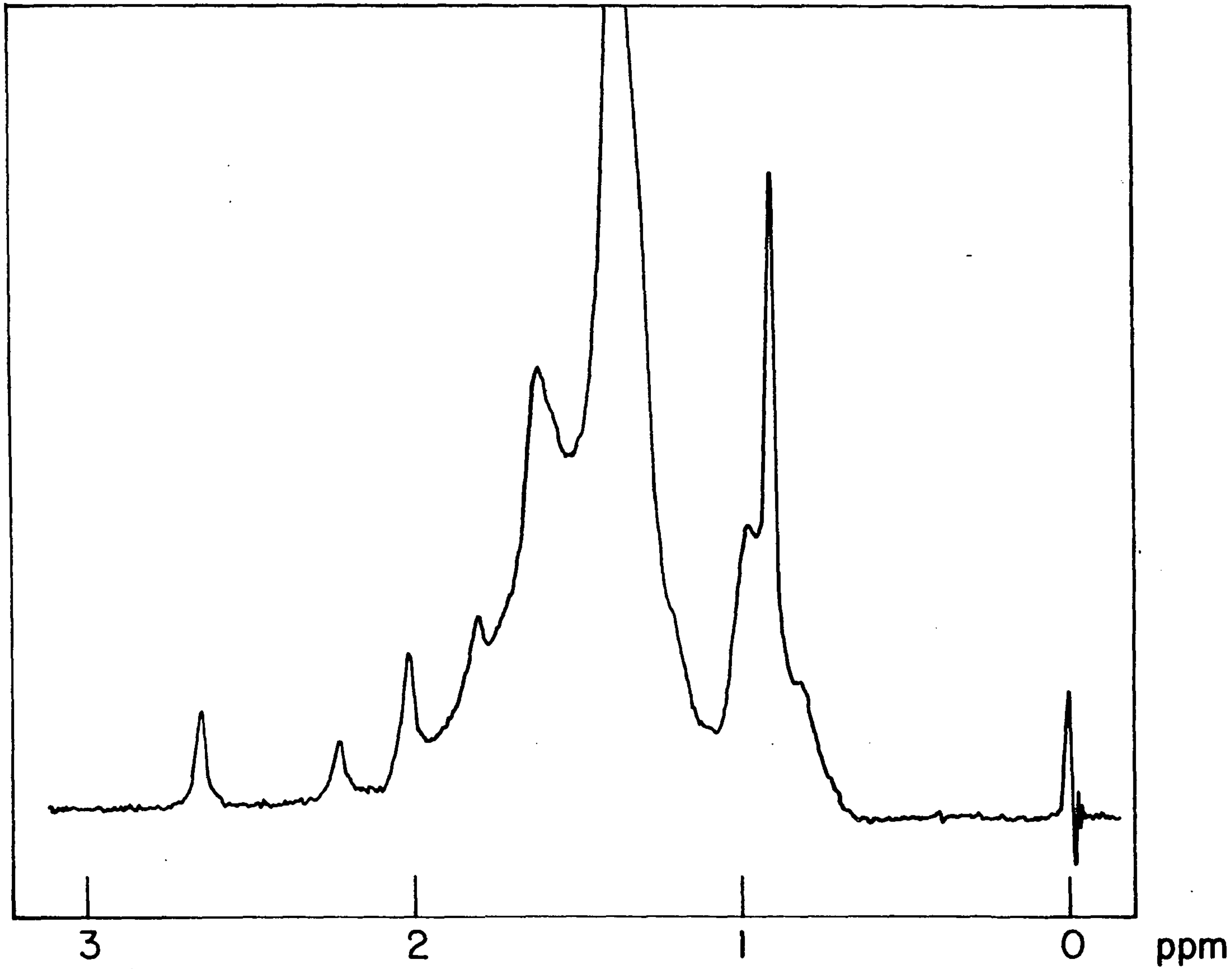
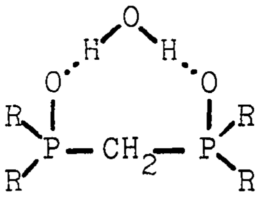


Figure 47. Nuclear magnetic resonance proton spectrum of partially dried HDPM in carbon tetrachloride

stability of this hydrated species and the fact that only a monohydrate seemed to be formed suggested the possibility of intramolecular hydrogen bonding with one water molecule bridging the two phosphoryl groups of a HDPM molecule. Additional water could enter the organic phase by hydrogen bonding



to the oxygen of this water molecule. This would explain the intensity of the band at 2.07 ppm; water-saturated carbon tetrachloride gives a barely discernible peak in this region.

The NMR spectra of water-saturated solutions of HDPP and HDPB in carbon tetrachloride had strong bands located at 3.44 and 3.54 ppm, respectively. A considerable increase in the amount of water extracted by these two compounds compared to that extracted by HDPM was shown by comparison of the band intensities of the hydroxyl protons with the protons of the terminal methyl groups. The relative sizes of these bands suggested dihydrate formation for HDPP and HDPB. Another important factor was the absence of a second band from the spectra. This meant that, if water in excess of the stoichiometric amount necessary to form the hydrated species was present, rapid proton exchange was occurring causing only a single band to appear in the spectrum.

A low intensity band was observed at 2.52 ppm for a water-saturated solution of TOPO in carbon tetrachloride. An area comparison of this band with the terminal methyl proton band indicated the H_2O/TOPO ratio was approximately 0.5. The nature of this species, if it is indeed a hydrate, is unknown although a convenient explanation would be two TOPO molecules hydrogen bonded to each water molecule.

The NMR spectrum of HDPE was not scanned because of the insolubility of this compound in carbon tetrachloride.

Infrared data

Infrared spectra of water-saturated solutions of the organophosphorus compounds in carbon tetrachloride or 1,2-dichloroethane seemed to confirm the hydrogen-bonding of water molecules to the phosphoryl oxygens. The band representing the vibrations of the phosphorus to oxygen bond was broadened considerably and shifted in the direction of lower frequencies in spectra of the water-saturated solutions (Table 35). A broad band, indicative of hydrogen-bonding, was observed in the 3100 to 3800 cm^{-1} region of each spectrum. The point of maximum absorbance of this band is reported in Table 35. Negligible absorbance was observed in this region of the spectrum for water-saturated carbon tetrachloride and only two small bands at 3600 and 3690 cm^{-1} were observed for water-saturated 1,2-dichloroethane. Very intense absorption was observed in the hydroxyl region of the spectra for water-saturated solutions of HDPP and HDPB in carbon tetrachloride. Somewhat lower intensities were found for the remaining three compounds and the absorbances of their hydroxyl bands followed the same order as the analytical data (Table 36) obtained for water-saturated solutions of these compounds in 1,2-dichlorobenzene.

Table 35. Phosphoryl and hydroxyl band frequencies for dried and water-saturated solutions of organophosphorus compounds

	Dry solutions	Water-saturated solutions	
Compound	P-O, cm^{-1}	P-O, cm^{-1}	OH, cm^{-1}
HDPM[a]	1176	1176-1172	3415
HDPE[b]	1165	1156	3380
HDPP[a]	1167	1160-1150	3400-3425
HDPB[a]	1167	1163-1156	3416
TOPO[b]	1164	1145-1155	3735

[a] 0.1 M in carbon tetrachloride.

[b] 0.1 M in 1,2-dichloroethane.

Chemical analyses

Equilibrations of 1,2-dichlorobenzene solutions of the five organophosphorus compounds (0.1 M) with water were conducted and the resultant organic phases were analyzed for water content by the Karl Fischer method (Table 36). A correction for

Table 36. Solubility of water in solutions of HDPM, HDPE, HDPP, and TOPO

Compound	Mole ratio, H_2O/Y
HDPM	0.96
HDPE	1.64
HDPP	2.09
HDPB	2.07
TOPO	0.65
TOPO[a]	0.62

Conditions: organophosphorus concentration-0.1 M
diluent-1,2-dichlorobenzene (unless otherwise indicated)

[a] Diluent-cyclohexane.

water solubility in 1,2-dichlorobenzene was determined by titration of an aliquot of the water-saturated diluent. The solubility of water in a 0.1 M solution of TOPO was also measured since it was reported by White and Ross (114) that less than one milligram of water per milliliter of solution could be detected in the organic phase after equilibration with water.

The data seemed to confirm formation of a monohydrate of HDPM and dihydrates of HDPP and HDPB. Mixed monohydrate and dihydrate formation seemed to be suggested by the HDPE data. The mole ratio obtained for TOPO did not rule out the formation of a dimer bridged by a water molecule.

Formation of the anhydrous monosolvated chelate, $UO_2(NO_3)_2 \cdot HDPM$, was confirmed by equilibration of a water-saturated, 0.1 M solution of HDPM ($HDPM \cdot H_2O$) in 1,2-dichlorobenzene with aqueous 1 M uranium(VI) nitrate. The water extracted by formation of the monohydrate was displaced by the formation of the uranium complex (Table 37).

Table 37. Displacement of water from $HDPM \cdot H_2O$ by uranium(VI) nitrate

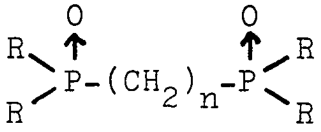
Water extracted by 1,2-dichlorobenzene	0.81 mg H_2O/ml
Water extracted by 0.1 M HDPM in 1,2-dichlorobenzene	2.53 mg H_2O/ml
Water extracted by 0.1 M HDPM[a] in 1,2-dichlorobenzene after equilibration with 1 M uranium(VI) nitrate	0.73 mg H_2O/ml

[a] Water saturated solution ($HDPM \cdot H_2O$)

The data appear to indicate the formation of discrete complexes, however the possibility of polymer formation can not be ruled out completely on the basis of these investigations alone.

SUMMARY

Organophosphorus compounds with the general formula,



where n = 2, 3 and 4 and R = n-hexyl, were synthesized and their solvent extraction properties were compared to those of gem-bis(di-n-hexylphosphinyl)methane (HDPM, n = 1) and tri-n-octyl phosphine oxide (TOPO). The nature of the specie (in solution) formed between uranium(VI) nitrate and HDPM, HDPE, HDPP, HDPB and TOPO was investigated by partition studies, infrared spectroscopy, conductivity and viscosity measurements. Hydrate formation by these organophosphorus compounds was investigated by the use of nuclear magnetic resonance proton spectra and chemical analyses.

Partition Studies

Solvent extraction of mineral acids

The organophosphorus compounds were, in order of increasing affinity for the mineral acids hydrochloric, nitric and perchloric acid, TOPO < HDPM < HDPE < HDPP < HDPB. Acid in excess of that required for the formation of a diprotonated species was extracted from higher concentrations of aqueous nitric acid by the bidentate organophosphorus compounds. This phenomena was also observed for extractions from 10 M hydrochloric acid. Stoichiometric amounts of acid, corresponding to the formation of a monoprotonated species for TOPO and the diprotonated species for HDPE, HDPP and HDPB were extracted from 10 M perchloric acid.

Solvent extraction of uranium

Bidentate organophosphorus compounds were found to be more powerful extractants of uranium(VI) than TOPO from hydrochloric, nitric and perchloric acid media. Partition studies indicated only small, regular differences among the organophosphorus compounds for extractions from hydrochloric and nitric acid. However, for extraction from perchloric acid, HDPM and HDPE (n = 1,2) exhibited distribution ratios which were orders of magnitude higher than those of HDPP, HDPB (n = 3,4) and TOPO. Presumably, the similarity in extraction behavior exhibited by the five compounds for extractions from hydrochloric and nitric acid was due in part to the coordinating abilities of these anions assisting in the formation of a extractable species. Extremely high distribution ratios for extraction from perchlorate media were explained by the postulation that the disolvates of HDPM and HDPE formed double chelate rings with each uranium being coordinated to four phosphoryl oxygens. Low distribution ratios obtained for HDPP, HDPB and TOPO were probably caused by the inability of these compounds to coordinate sufficient phosphoryl oxygens to the uranium atom to saturate its coordination positions. Since perchlorate is a non-coordinating anion, water probably would fill the unoccupied coordination position or positions. This would tend to depress extraction since a more hydrophilic species would be formed.

Solvent extraction of some lanthanides

Extraction of praseodymium, neodymium, samarium and thulium from nitrate, chloride and perchlorate media was investigated to evaluate the bidentate organophosphorus compounds HDPM, HDPE, HDPP and HDPB as possible means of separating adjacent lanthanide elements.

Extractions from hydrochloric and nitric acids indicated no significant differences in extraction behavior among the bidentate organophosphorus compounds. The greatest differences in extraction were again noted in comparing extractions from perchloric acid. Distribution ratios for HDPM remained relatively high (2 to 10) over the complete range of acid concentrations studied (0.1 to 7 $\underline{M}$) whereas extraction with HDPE dropped off considerably when the acid concentration was increased above 0.1 $\underline{M}$. Distribution ratios were generally very low (≤ 0.6) for HDPP and HDPB for all acid concentrations.

Separation factors (ratio of individual distribution ratios for different elements under the same extraction conditions) were very low for adjacent lanthanide elements over the acid concentration ranges studied and thus the use of these compounds alone as a means of separating adjacent lanthanides was not very promising.

Synergistic enhancement of distribution ratios was studied briefly for the systems, thenoyltrifluoroacetone (TTA)-HDPM (HDPE) and praseodymium. A tremendous enhancement effect was noted for 0.1M TTA-0.05M HDPM (HDPE) mixtures with Pr maintained at 0.167 M in low concentrations ($\leq 10^{-2}$ M) of perchloric acid. An enhancement was also noted for extraction from nitrate media but it was considerably smaller in magnitude.

Nature of the Complexes Formed Between Uranium(VI) Nitrate and HDPM, HDPE, HDPP, HDPB and TOPO

Partition studies

The logarithmic dependance of distribution ratio on solvent concentration was investigated at high ligand/metal ratios (15 to 1000:1) in order to obtain definitive information about the stoichiometry of the higher complexes formed in organic solution between uranium and the organophosphorus compounds, HDPM, HDPE, HDPP, HDPB and TOPO. These studies indicated that the disolvated complexes of HDPM and HDPE were the principal specie in solution for ligand/metal ratios in excess of 2:1. Non-integral numbers were obtained for the logarithmic dependance of distribution ratio on HDPP and HDPB concentration with a value of 1.6 observed for HDPP and 1.5 for HDPB. These data were not very meaningful in terms of a solvation number for the higher complexes of these two compounds. The data for TOPO indicated that a trisolvated complex was formed at high ligand/metal ratios. This trisolvate of uranium(VI) nitrate and TOPO has not been previously reported in the literature.

Saturation experiments conducted with uranium(VI) nitrate indicated that the lower complex (in the presence of an aqueous phase) was a monosolvate for the bidentate organophosphorus ligands and a disolvate for TOPO. Uranium in excess of that required for a monosolvate (disolvate for TOPO) was dissolved in the organic phase when uranium(VI) nitrate dihydrate was used as the saturating medium (in the absence of an aqueous phase). This indicated partial monosolvate formation for TOPO and, by analogy, partial formation of hemisolvated bidentate complexes of HDPM, HDPE, HDPP and HDPB.

The conditional equilibrium constant for the disolvate of HDPM and uranium(VI) nitrate (calculated for extractions from 1 $\underline{M}$ nitric acid) was related to the constant obtained for extractions from low acid concentration solutions (10^{-3} $\underline{M}$) by calculating the reduction in free ligand concentration by acid complexation. This illustrated a relation between acid competition and depression of distribution ratios for these particular conditions.

Infrared studies

Coordination via the phosphoryl oxygen to uranium decreased the P-O stretching frequency, presumably because of a decrease in $p\pi \rightarrow d\pi$ back-bonding from the electron-rich p orbitals of oxygen to the electron-deficient d orbitals of phosphorus (22). The absorbance of the various complexed phosphoryl bands were plotted as a function of uranium(VI) nitrate concentration. These data appeared to confirm formation of monosolvated complexes for all five organophosphorus compounds and disolvated complexes for HDPM, HDPE, HDPP and TOPO. No evidence of disolvate formation was observed for HDPB; the data appeared to be best explained by postulation of a sesquisolvated bidentate complex with one HDPB molecule bridging two uranium atoms and with a second HDPB molecule coordinated through both phosphoryl oxygens to each uranium. Mixed monosolvate and disolvate formation was indicated by the infrared spectra of HDPP-uranium solutions. These data were interpreted as indicating that chelate ring formation with the second molecule of HDPP ($n = 3$) was, at best, difficult and it appeared to be impossible in the case of HDPB ($n = 4$). The formation of a trisolvated complex, $UO_2(NO_3)_2 \cdot 3TOPO$, appeared to be confirmed for this monodentate ligand.

The presence of ionic nitrate and the very slow rate of increase in covalent nitrate (followed by plotting the absorbance of the asymmetric stretching frequency of the covalent nitrato group against uranium concentration) were interpreted as indicating complete displacement of nitrate from the coordination sphere of uranium in the presence of HDPM and HDPE in excess of a 2.6:1 ligand/uranium ratio. The data for HDPP and HDPB showed simultaneous increases in both covalent and ionic nitrate concentrations thus indicating that either both nitrate groups were not displaced from the coordination sphere or mixtures of complexes were being formed.

Trisolvate formation for TOPO would be expected to result in the displacement of one nitrate group from the coordination sphere of uranium. A small band was noted in the ionic nitrate region of the spectrum at high ligand/metal ratios apparently confirming formation of a small but significant concentration of this complex.

Conductivity and viscosity studies

Molar conductivity measurements for varying ratios of ligand/metal (nitrobenzene solution) were characterized by sharp minima at 1:1 ratios for the four bidentate organophosphorus compounds and at a 2:1 ratio for TOPO, a monodentate ligand. This signified formation of highly covalent specie at these molar ratios apparently confirming formation of chelate ring complexes for the monosolvates of the bidentate organophosphorus compounds although it did not completely rule out the possibility of polymer formation. Increasing molar conductivities were observed as the ligand/metal ratios increased, seemingly confirming ionization of the nitrate groups as indicated in the infrared spectra.

Viscosities were observed to decrease with decreasing ligand/metal ratios for HDPM and HDPB. These data appeared to support formation of discrete complexes rather than formation of polymeric species and furnished additional evidence in favor of a chelate structure for the monosolvates of all bidentate organophosphorus compounds.

Hydrate Formation for HDPM, HDPE, HDPP, HDPB and TOPO

Nuclear magnetic resonance spectra, infrared spectra and water solubility determinations suggested the possibility of hydrate formation for the five organophosphorus solvents. The additional stability and the NMR spectrum of $HDPM\cdot H_2O$ were interpreted as indicating a intramolecular hydrogen-bonded structure with one water molecule bonded to both phosphoryl oxygens of a single HDPM molecule. Mixed monohydrate and dihydrate formation was indicated for HDPE while only dihydrate formation was thought to occur for HDPP and HDPB from water solubility data for these compounds. A ratio of 0.6 water molecule per TOPO molecule was determined by analysis of water-saturated solutions of this compound in two different diluents. A possible structure might involve a dimeric species with two TOPO molecules bridged by a single water molecule, however, polymer formation cannot be ruled out as a possibility here and also in the cases of the bidentate ligands.

BIBLIOGRAPHY

1. Ahrland, S. *Acta Chem. Scand.* 5, 1271. 1951.

2. Alcock, K., Best, G. G., Hesford, E. and McKay, H. A. C. *J. Inorg. Nucl. Chem.* *6*, 328. 1958.

3. Alcock, K., Grimley, S. S., Healy, T. V., Kennedy, J. and McKay, H. A. C. *Trans. Faraday Soc.* 52, 39. 1956.

4. Allpress, J. G. and Hambly, A. N. *Australian J. Chem.* 12, 569. 1959.

5. Axtmann, R. C. *Nuclear Sci. Eng.* *16*, 241. 1963.

6. Baes, C. F., Jr. *J. Inorg. Nucl. Chem.* *24*, 707. 1962.

7. Banerjea, D. and Tripathi, K. K. *J. Inorg. Nucl. Chem.* *18*, 199. 1961.

8. Barney, J. E., II, Bergmann, J. G. and Tuskan, W. G. *Anal. Chem.* *31*, 1394. 1959.

9. Best, G. F., Hesford, E. and McKay, H. A. C. *J. Inorg. Nucl. Chem.* *12*, 136. 1959.

10. Betts, R. H. and Michels, R. K. *J. Chem. Soc.* *1949*, s-286. 1949.

11. Bjerrum, N. and Jozefowicz, E. *Z. Phys. Chem.* *A-159*, 194. 1932.

12. Bjerrum, N. and Larsson, E. *Z. Phys. Chem.* *127*, 358. 1927.

13. Blake, C. A., Baes, C. F., Brown, K. B., Coleman, C. F. and White, J. C. International Conference on the Peaceful Uses of Atomic Energy, 2nd, Geneva, 1958, Proceedings *28*, 289. 1959.

14. Blake, C. A., Brown, K. B. and Coleman, C. F. *U. S. Atomic Energy Commission Report ORNL-1964* [Oak Ridge National Lab., Tenn.]. 1955.

15. Blake, C. A., Moore, J. G. and Whaley, W. M. *U. S. Atomic Energy Commission Report ORNL-1480* [Oak Ridge National Lab., Tenn.]. 1952.

16. Brand, J. D. and Cawthon, T. M. *J. Am. Chem. Soc. 77*, 319. 1955.

17. Bullock, E. and Tuck, D. G. *Trans. Faraday Soc. 59*, 1293. 1963.

18. Burger, L. L. *U. S. Atomic Energy Commission Report HW-44888* [Hanford Atomic Products Operation, Richland, Wash.]. 1957.

19. Burger L. L. *J. Phys. Chem. 62*, 590. 1958.

20. Collopy, T. J. and Blum, J. F. *J. Phys. Chem. 64*, 1324. 1960.

21. Collopy, T. J. and Cavendish, J. H. *J. Phys. Chem. 64*, 1328. 1960.

22. Cotton, F. A., Barnes, R. D. and Bannister, E. *J. Chem. Soc. 1960*, 2199. 1960.

23. Cuninghame, J. G., Scargill, P. and Willis, H. H. *U. S. Atomic Energy Commission Report AERE-C/M-215* [Gt. Brit. Atomic Energy Research Establishment, Harwell, Berks, England]. 1954.

24. Daasch, L. W. and Smith, D. C. *Anal. Chem. 23*, 853. 1951.

25. Day, R. A., Jr. and Powers, R. M. *J. Am. Chem. Soc. 76*, 3895. 1954.

26. Diamond, R. M. and Tuck, D. G. Progress in inorganic chemistry. Vol. *2*. New York, N. Y., Interscience Publishers, Inc. c1960.

27. Fajan, V. K. *Naturwiss. 11*, 165. 1923.

28. Feder, H. M., Ross, L. E. and Vogel, R. C. *U. S. Atomic Energy Commission Report ANL-4868* [Argonne National Lab., Lemont, Ill.]. 1952.

29. Ferguson, J. W., Richard, J. J., O'Laughlin, J. W. and Banks, C. V. [Simultaneous spectrophotometric determination of calcium and magnesium with chlorophosphonazo III.] [To be published in *Anal. Chem. ca.* 1964.]

30. Ferraro, J. R. *J. Inorg. Nucl. Chem. 10*, 319. 1959.

31. Ferraro, J. R. *J. Mol. Spectroscopy* *4*, 99. 1960.

32. Fletcher, J. M. Progress in nuclear energy, series 3, process chemistry. Vol. *1*. London, Pergamon Press Ltd. 1956.

33. Foulk, C. W. and Bawden, A. T. *J. Am. Chem. Soc.* *48*, 2045. 1926.

34. Fritz, J. S. and Hammond, G. S. Quantitative organic analysis. New York, N. Y., J. Wiley and Sons. c1957.

35. Fritz, J. S. and Johnson-Richard, M. *Anal. Chim. Acta* *20*, 164. 1959.

36. Gatehouse, B. M., Livingstone, S. E. and Nyholm, R. S. *J. Chem. Soc.* *1957*, 4222. 1957.

37. Gore, R. C. *Discussions Faraday Soc.* *9*, 138. 1950.

38. Hardy, C. J., Greenfield, B. F. and Scargill, D. *J. Chem. Soc.* *1961*, 90. 1961.

39. Healy, T. V. and Kennedy, J. J. *J. Inorg. Nucl. Chem.* *10*, 128. 1959.

40. Healy, T. V. and McKay, H. A. C. *Trans. Faraday Soc.* *52*, 633. 1956.

41. Herzberg, G. Molecular spectra and molecular structure. [Vol.] *2*: Infrared and Raman spectra of polyatomic molecules. New York, N. Y., D. Van Nostrand Company, Inc. 1945.

42. Hesford, E., Jackson, E. E. and McKay, H. A. C. *J. Inorg. Nucl. Chem.* *9*, 279. 1959.

43. Hesford, E. and McKay, H. A. C. *J. Inorg. Nucl. Chem.* *13*, 165. 1960.

44. Hesford, E. and McKay, H. A. C. *Trans. Faraday Soc.* *54*, 573. 1958.

45. Higgins, C. E. and Baldwin, W. H. *Anal. Chem.* *32*, 233. 1960.

46. Higgins, C. E., Baldwin, W. H. and Soldano, B. A. *J. Phys. Chem.* *63*, 113. 1959.

47. Irani, R. R. and Moedritzer, K. *J. Phys. Chem. 66*, 1349. 1962.

48. Irving, H. and Edgington, D. N. *Proc. Chem. Soc. (London) 1959*, 360. 1959.

49. Ishimori, T., Kimura, K., Fujino, T. and Murakami, H. *J. Atomic Energy Soc. Japan 4*, 117. 1962.

50. Ishimori, T. and Watanabe, K. *Bull. Chem. Soc. Japan 33*, 1443. 1960.

51. Ishimori, T., Watanabe, K. and Nakamura, E. *Bull. Chem. Soc. Japan 33*, 636. 1960.

52. Johnson, W. F. and Dillon, R. L. *U. S. Atomic Energy Commission Report HW-29086* [Hanford Atomic Products Operation, Richland, Wash.]. 1953.

53. Jones, L. H. *Spectrochim. Acta 6*, 409. 1959.

54. Kaplan, L., Hildebrandt, R. A. and Ader, M. *J. Inorg. Nucl. Chem. 2*, 153. 1956.

55. Katzin, L. L. *J. Chem. Phys. 18*, 789. 1950.

56. Katzin, L. I. *J. Inorg. Nucl. Chem. 20*, 300. 1961.

57. Katzin, L. I. *J. Inorg. Nucl. Chem. 24*, 245. 1962.

58. Kertes, A. S. and Halpern, M. *J. Inorg. Nucl. Chem. 19*, 359. 1961.

59. Kertes, A. S. and Halpern, M. *J. Inorg. Nucl. Chem.* 20, 117. 1961.

60. Kinney, P. J. An infrared study of the tributyl phosphate-nitric acid-water solvent extraction system. Unpublished Ph.D. thesis. Ames, Iowa, Library, Iowa State University of Science and Technology. 1963.

61. Knizakova, E. and Korbl, J. *Chem. listy* 52, 750. 1958.

62. Komarov, E. V. and Shuvanlov O. N. *Radiokhim. 4*, 543. 1962. Original not available; abstracted in *Nuclear Science Abstracts 17*, 20114. 1963.

63. Kosolapoff, G. M. and Struck, R. F. *J. Chem. Soc. 1961*, 2423. 1961.

64. Kraus, K. A., Moore, G. E. and Nelson, F. *J. Am. Chem. Soc. 78*, 2692. 1956.

65. Kraus, K. A. and Nelson, F. International Conference on the Peaceful Uses of Atomic Energy, [1st], Geneva, 1955, Proceedings *7*, 118. 1956.

66. Larsson, L. *Svensk Kem. Tidskr. 71*, 336. 1959.

67. Lysyj, I. and Zarembo, J. *Microchem. J. 2*, 245. 1958.

68. Madigan, D. C. and Cattrall, R. W. *J. Inorg. Nucl. Chem. 21*, 334. 1961.

69. Marcus, Y. *Chem. Rev. 63*, 139. 1963.

70. Morrison, G. H. and Freiser, H. *Anal. Chem.* 34, 64R. 1962.

71. Mrochek, J. E., O'Laughlin, J. W., Sakurai, H. and Banks, C. V. *J. Inorg. Nucl. Chem. 25*, 955. 1963.

72. Murray, B. B. and Axtmann, R. C. *Anal. Chem. 31*, 450. 1959.

73. Nadig, E. Metal nitrate complexes with tributyl phosphate and with trioctyl phosphine oxide. Unpublished Ph.D. thesis. Ames, Iowa, Library, Iowa State University of Science and Technology. 1963.

74. Naito, K. and Suzuki, T. *J. Phys. Chem. 66*, 989. 1962.

75. Nemodruk, A. A., Novikov, Y. P., Lukin, A. M. and Kalinina, I. D. *J. Anal. Chem. U. S. S. R. 16*, 187. 1961.

76. New organophosphorus reagents debut. *Chemical Eng. News 38*, No. 38, 57. 1960.

77. Nickolaev, A. V. and Sorakina, A. A. *Dokl. Akad. Nauk S. S. S. R.* 129, 341. 1959.

78. Nomura, S. and Hara, R. *Anal. Chim. Acta 25*, 212. 1961.

79. Nukada, K., Naito, K. and Maeda, U. *Bull. Chem. Soc. Japan 33*, 894. 1960.

80. Olander, D. R., Donadieu, L. and Benedict, M. *A.I.Ch.E. Journal 7*, 152. 1961.

81. O'Laughlin, J. W. Separation of various cations by reversed-phase partition chromatography using neutral organophosphorus compounds. Unpublished Ph.D. thesis. Ames, Iowa, Library, Iowa State University of Science and Technology. 1963.

82. O'Laughlin, J. W., Sealock, F. W. and Banks, C. V. [Determination of solubility of several phosphine oxides in aqueous solutions using a new spectrophotometric procedure.] [To be published in Anal. Chem. ca. 1964.]

83. Oshima, K. J. Atomic Energy Soc. Japan 4, 8. 1962.

84. Oshima, K. J. Atomic Energy Soc. Japan 4, 166. 1962.

85. Peppard, D. F., Driscoll, W. J., Sironen, R. J. and McCarty, S. J. Inorg. Nucl. Chem. 4, 326. 1957.

86. Peppard, D. F. and Ferraro, J. R. J. Inorg. Nucl. Chem. 15, 365. 1960.

87. Redlich, O. and Bigeleisen, J. J. Am. Chem. Soc. 65, 1883. 1943.

88. Richard, J. J. and Banks, C. V. J. Org. Chem. 28, 123. 1963.

89. Richard, J. J., Burke, K. E., O'Laughlin, J. W. and Banks, C. V. J. Am. Chem. Soc. 83, 1722. 1961.

90. Robinson, R. A. and Stokes, R. H. Electrolyte solutions. New York, N. Y., Academic Press, Inc. 1955.

91. Saisho, H. Bull. Chem. Soc. Japan 34, 859. 1961.

92. Saisho, H. Bull. Chem. Soc. Japan 34, 1254. 1961.

93. Sandell, E. B. Colorimetric determination of traces of metals. 3rd ed. New York, N. Y., Interscience Publishers, Inc. 1959.

94. Scargill, D., Alcock, K., Fletcher, J. M., Hesford, E. and McKay, H. A. C. J. Inorg. Nucl. Chem. 4, 304. 1957.

95. Seaborg, G. T. The transuranium elements. New Haven, Conn., Yale University Press. c1958.

96. Shevchenko, V. B., Shilin, I. V. and Solovkin, A. S. Russ. J. Inorg. Chem. 3, 347. 1958.

97. Siddall, T. H., III. *Ind. Eng. Chem.* *51*, 41. 1959.

98. Siddall, T. H., III. *J. Inorg. Nucl. Chem.* *25*, 883. 1963.

99. Siekierski, S. *J. Inorg. Nucl. Chem.* *12*, 129. 1959.

100. Siekierski, S. *J. Inorg. Nucl. Chem.* *24*, 205. 1962.

101. Siekierski, S. and Fidelis, I. *J. Chromatog.* *4*, 60. 1960.

102. Small, H. *J. Inorg. Nucl. Chem.* *19*, 160. 1961.

103. Solovkin, A. S., Konorev, M. I. and Adaev, D. P. *Russ. J. Inorg. Chem.* *5*, 903. 1960.

104. Taube, M. *J. Inorg. Nucl. Chem.* *12*, 174. 1959.

105. Tuck, D. G. *J. Chem. Soc.* *1958*, 2783. 1958.

106. Tuck, D. G. *Trans. Faraday Soc.* *57*, 1297. 1961.

107. Tuck, D. G. and Diamond, R. M. *J. Phys. Chem.* *65*, 193. 1961.

108. Vdovenko, V. M., Lipkovskii, A. A. and Nikitina, S. A. *Radiokhim.* *5*, 139. 1963. Original not available for examination; abstracted in *Nuclear Science Abstracts* *17*, 25328. 1963.

109. Vdovenko, V. M., Lipkovskii, A. A. and Nikitina, S. A. *Russ. J. Inorg. Chem.* *4*, 391. 1959.

110. Vdovenko, V. M., Lipovskii, A. A. and Nikitina, S. A. *Russ. J. Inorg. Chem.* *5*, 449. 1960.

111. Vogel, A. I. A textbook of practical organic chemistry including qualitative organic analysis. New York, N. Y., Longmans, Green and Co. 1948.

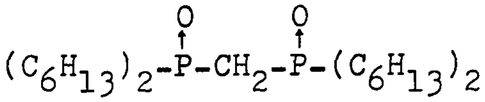
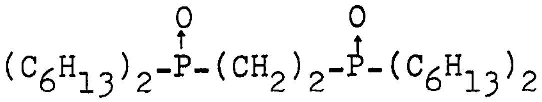
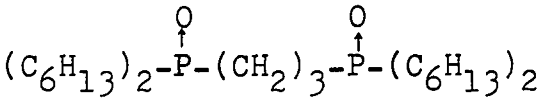
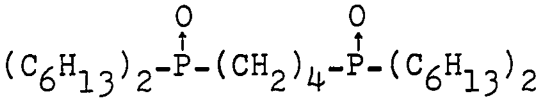
112. Warf, J. C. *J. Am. Chem. Soc.* *71*, 3257. 1949.

113. Welcher, F. J. The analytical uses of ethylenediamine tetraacetic acid. Princeton, N. J., D. Van Nostrand Company, Inc. c1958.

114. White, J. C. and Ross, W. J. _U. S. Atomic Energy Commission Report NAS-NS-3102_ [National Academy of Sciences]. 1961.

115. Whitney, D. C. and Diamond, R. M. _J. Phys. Chem._ _67_, 209. 1963.

APPENDIX

Tri-*n*-butyl phosphate	TBP	$(C_4H_9O)_3-P\rightarrow O$
Tri-*n*-octyl phosphine oxide	TOPO	$(C_8H_{17})_3-P\rightarrow O$
Bis(di-*n*-hexyl-phosphinyl)methane	HDPM	 $(C_6H_{13})_2-\overset{\overset{O}{\uparrow}}{P}-CH_2-\overset{\overset{O}{\uparrow}}{P}-(C_6H_{13})_2$
Bis(di-*n*-hexyl-phosphinyl)ethane	HDPE	 $(C_6H_{13})_2-\overset{\overset{O}{\uparrow}}{P}-(CH_2)_2-\overset{\overset{O}{\uparrow}}{P}-(C_6H_{13})_2$
Bis(di-*n*-hexyl-phosphinyl)propane	HDPP	 $(C_6H_{13})_2-\overset{\overset{O}{\uparrow}}{P}-(CH_2)_3-\overset{\overset{O}{\uparrow}}{P}-(C_6H_{13})_2$
Bis(di-*n*-hexyl-phosphinyl)butane	HDPB	 $(C_6H_{13})_2-\overset{\overset{O}{\uparrow}}{P}-(CH_2)_4-\overset{\overset{O}{\uparrow}}{P}-(C_6H_{13})_2$

ACKNOWLEDGMENTS

The author would like to express his deep appreciation to his wife, Shirley, for her sacrifices and encouragement which made this work possible. The cooperation and counseling of Dr. C. V. Banks are gratefully acknowledged. The assistance of Mr. James R. Birk, Mr. Richard Hamilton and Mr. Denny Carlson in some of the experimental work was appreciated. The author would also like to thank Dr. J. W. O'Laughlin, Mr. John J. Richard, Mr. Richard N. Kniseley and Mr. James R. Parker for their assistance and helpful discussions.