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A Study of the Kinetics and the Free Radicals Involved in the Low-Pressure, Vapor-Phase Pyrolysis of Toluene

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THE
EXTRACTIO
OF
SCANDIUM

WARREN

THE EXTRACTION OF SCANDIUM, YTTRIUM, AND LANTHANUM USING VARIOUS MONOALKYL ORTHOPHOSPHORIC ACIDS

A Dissertation
Presented to
the Faculty of the Graduate School
University of New Mexico

In Partial Fulfillment
of the Requirements for the Degree
Doctor of Philosophy

by
Clarence Gerald Warren
June 1958

This dissertation, directed and approved by the candidate's committee, has been accepted by the Graduate Committee of the University of New Mexico in partial fulfillment of the requirements for the degree of

DOCTOR OF PHILOSOPHY

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DATE May 30, 1958

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Dean

May 30, [illegible]

Date

Committee

Chairman

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I. INTRODUCTION

The separation of lanthanum, yttrium, and the rare earth elements from their ores has been a challenge to the chemist for many years. The similarity in chemical properties has made their separation a problem of extraordinary difficulty. Fractional crystallization has been the classical method utilized in the past, although individual elements have been isolated by oxidation or reduction to other than the tripositive oxidation state (1). Recently ion exchange and solvent extraction methods have become more important as a means of separation of these elements. Both of these techniques depend upon fractional differences in the distribution of compounds or ions of the rare earth elements between two phases (2). For both methods, the equivalent of many single stage separations is combined through the use of present-day experimental techniques eliminating much of the tedious work required by fractional crystallization. Solvent extraction procedures have the additional advantage of continuous operation by use of an automatic extraction apparatus (3).

Although there are a number of sparingly soluble salts of the rare earths, only a few have been extensively utilized for separation procedures. The double salt of magnesium nitrate and the rare earth nitrate has been used

for the separation of the cerium group[1] and the bromate or the dimethyl phosphate (1) salts have been used for the separation of the yttrium group.[2] Each crystallization resulted in a slight enrichment of heavier elements in the mother liquor. In the original separation of ytterbium and lutetium 15,000 crystallizations were made (4). With the exception of the dimethyl phosphate derivatives all salts of the rare earths increase in solubility with increasing atomic number. Since the abundance of the rare earth elements decreases in the same order, the difficulty of obtaining the higher members as pure crystalline compounds is magnified. Thus, the necessity of developing procedures dependent upon other properties of these elements is apparent.

Newer separation procedures utilize the relative tendencies of the metal ion to combine with a complexing reagent (5). Two main factors govern the stability of these metal complexes: charge density which depends upon ionic charge and radius of the metal ion (6), and the tendency of the metal to form covalent bonds (7). All of the rare earth

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[1] The cerium group includes elements from atomic number 57 to 62.

[2] The yttrium group includes yttrium and elements from atomic number 63 to 71.

elements, scandium, and yttrium have a stable tripositive oxidation state and form similar type compounds so that only the effect of ionic radius on compound stability need be considered. The radius of the tripositive rare earth ions decreases with increasing atomic number (1). Thus cerium ion (Z=58) has a radius of 1.18A, lutetium ion (Z=71) has a radius of 0.99A, and the other rare earth ions lie in between. The radii of the group IIIa ions bracket the ionic radius of the rare earth elements. Thus scandium ion has a radius of 0.83A, lanthanum ion has a radius of 1.22A, and yttrium has an intermediate value (5). The stability of the complexes increases as ionic radius of the metal ion decreases.

In ion exchange separations of the rare earths (8), a mixture of these ions is absorbed from an acid solution at the top of a column packed with a cation exchange resin. The column is then eluted at a controlled pH with a complexing agent such as ammonium citrate. Under these conditions a series of competitive reactions is established between the complex ions in solution and the ions on the exchange resin. The smaller ions form stronger aqueous complexes and are eluted first. The cation forming the least stable aqueous complex emerges from the column last.

Solvent extraction separation of the rare earths (2) depends upon the preferential extractability of their compounds in water-immiscible solvents. A class of reagents which form

readily extractable complexes with the rare earth elements are the phosphate esters. For example, tributyl phosphate and various dialkyl hydrogen phosphates (9) have been utilized to separate the rare earths. The basic chemistry of the extraction of the rare earths by the alkyl phosphates is not completely understood. With this in mind an investigation was made of the effect of the monoalkyl phosphoric acids upon the extraction of scandium, yttrium, and lanthanum. The chain length of the alkyl groups was varied to study the effect on the extraction agents.

II. DISCUSSION

The chemistry basic to the various topics covered in this work is discussed in this section, and only the material which pertains directly to the problem or is necessary for a logical presentation is included. The topics covered include chemistry of phosphoric acid, chemistry of the alkyl phosphoric acids, the principles of solvent extraction, and the chemistry of the group IIIa elements.

The Chemistry of the Phosphoric Acids

The monoalkyl phosphoric acids are derivatives of phosphoric acid and the chemistry of the two is closely related. The following discussion of the chemistry of phosphoric acid includes information pertinent to the chemistry of the alkyl phosphates.

Three phosphoric acids (10, 11, 12) are known; ortho-, H_3PO_4; pyro-, $H_4P_2O_7$; and metaphosphoric acid, $(HPO_3)_n$. Metaphosphoric acid has various forms, and n can have a value of three or larger. The meta- and pyrophosphoric acids are condensed acids and are formed by elimination of water from the ortho form. Solutions containing less than 72 percent phosphoric oxide, at equilibrium, consist mostly of the orthophosphoric acid. However, solutions of the same concentration prepared from the meta or pyro acid can be kept for days because equilibrium conditions are attained slowly (12). Acid conditions and elevated temperature accelerate the attainment of equilibrium conditions.

$$H_4P_2O_7 + H_2O \underset{H^+}{\rightleftharpoons} 2H_3PO_4$$

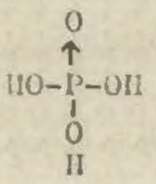
In a solution of one molar hydrogen ion, pyrophosphoric acid is 50 percent hydrolyzed to orthophosphoric acid in 16 hours at 40° C. or 72 hours at 20°C. Neutral or alkaline solutions (13) of pyrophosphoric acid are relatively stable with respect to hydrolysis even at room temperature. For example, sodium pyrophosphate dissolves in water to form a stable solution.

Elevated temperatures are required for the formation of the condensed acids. Below 149°C. orthophosphoric acid is the stable form. Between 149°C. and 160°C., a small

amount of pyrophosphoric acid is formed. Although the pyro acid is the principle product at 212°C., the temperature must be raised to 255° - 260°C. to obtain pure pyrophosphoric acid. Between 290°C. and 300°C. metaphosphoric acid begins to form.

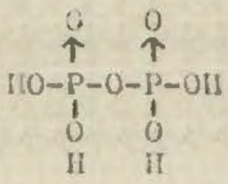
The melting points of the crystalline phosphoric acids (12) are as follows: H_3PO_4, 42.4°C.; $(H_3PO_4)_2 \cdot H_2O$, 30°C.; $H_4P_2O_7$, 61°C.

The structures of the phosphoric acids are based upon the PO_4 tetrahedra (14). In the condensed forms, an oxygen atom is shared by adjacent phosphorus atoms. Either chains or rings of alternating phosphorus and oxygen atoms can be formed.



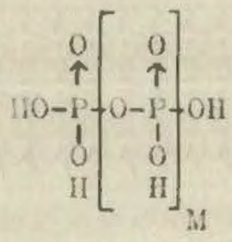
$HO-\overset{\overset{O}{\uparrow}}{\underset{\underset{H}{O}}{P}}-OH$

Orthophosphoric
acid



$HO-\overset{\overset{O}{\uparrow}}{\underset{\underset{H}{O}}{P}}-O-\overset{\overset{O}{\uparrow}}{\underset{\underset{H}{O}}{P}}-OH$

Pyrophosphoric
acid



$HO-\overset{\overset{O}{\uparrow}}{\underset{\underset{H}{O}}{P}}\left[-O-\overset{\overset{O}{\uparrow}}{\underset{\underset{H}{O}}{P}}-\right]_M OH$

Metaphosphoric
acid

Comparison of the ionization constants of the pyro and ortho acids shows that pyrophosphoric acid is the stronger of the two. This behavior is also observed when oxyacids of other elements polymerize. Numerous workers (15) have reported that, in solution, there is at least one strong acid group for each phosphorus atom regardless of the particular phosphoric acid considered. The other acid groups

are less acidic and are neutralized by salt formation at a high pH. The first hydrogen for each phosphorus atom is neutralized between pH 3.8 to 4.2 regardless of the species present in aqueous solution.

Preparation and Properties of the Alkyl Phosphates

The extraction reagents, the alkyl phosphoric acids, were not commercially available with the purity desired. A brief resume of generally accepted preparations of these compounds and their properties is included so that the problems encountered in their synthesis and purification can be appreciated.

The classical preparation of the alkyl phosphates by the reaction of alcohol with phosphorus pentoxide presents a number of problems in the separation of the products. Among the products are phosphoric acid and its esters, the mono-, di-, and trialkyl phosphates as well as derivatives of the condensed forms of phosphoric acid. The condensed phosphoric acids are eliminated by heating with an excess of water. The reaction of phosphoric oxide and alcohol is usually represented by the following equation because the primary and secondary esters predominate (16):

$$3ROH + P_2O_5 \longrightarrow RO(HO)_2PO + (RO)_2(HO)PO$$

where R = an alkyl group

The mixture can be separated by fractional precipitation of an appropriate salt of the alkyl phosphoric acid or by sol-

vent extraction procedures (17). For example, the barium salt of the primary ester is less soluble than the corresponding salt of the secondary ester. Separation by fractional precipitation is satisfactory for esters with small alkyl groups, but it becomes laborious for the higher derivatives since the salts of both the primary and secondary esters of these derivatives are sparingly soluble. Distillation can not be used for separation because of thermal decomposition. The separation of the secondary and primary esters by liquid-liquid extraction depends upon the preferential solubility of the secondary esters for the organic phase. This method has been used to purify the dialkyl phosphates for use in solvent extraction studies by a number of workers (18).

Another common method used to prepare the alkyl phosphates is the hydrolysis of the alkyl chlorophosphates (16) as the following equations indicate:

$$(RO)Cl_2PO + 2H_2O \longrightarrow (RO)(HO)_2PO + 2HCl$$

$$(RO)_2ClPO + H_2O \longrightarrow (RO)_2(HO)PO + HCl$$

The alkyl dichlorophosphates with small alkyl groups can be hydrolyzed by water at room temperature, but the derivatives with larger alkyl groups require either elevated temperatures, basic solutions, or both. The dialkyl chlorophosphates follow the same trend but are more difficult to hydrolyze than

the monoalkyl chlorophosphates. Some organochlorophosphates containing large organic groups are so difficult to hydrolyze that formation of the phosphate by this method is not feasible (19). Purification of the chlorophosphates must precede the hydrolysis in order to obtain pure products. The conditions under which the hydrolysis reaction is carried out is critical. For example, the hydrolysis of the dialkyl chlorophosphates with a limited amount of water produces the pyrophosphate (19).

$$2(RO)_2POCl + H_2O \longrightarrow R_4P_2O_7 + 2HCl$$

The chlorophosphate esters are prepared by the reaction of phosphorus oxychloride and the corresponding alcohol (16). A series of products are obtained:

$$ROH + POCl_3 \longrightarrow (RO)Cl_2PO + HCl$$

$$2ROH + POCl_3 \longrightarrow (RO)_2ClPO + 2HCl$$

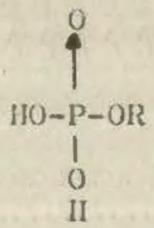
$$3ROH + POCl_3 \longrightarrow (RO)_3PO + 3HCl$$

The reactivity of the alkyl chlorophosphate decreases with the number and size of the alkyl groups attached so that by careful control of the reactant concentrations, undesired products are largely eliminated. However, it is impossible to completely eliminate side reactions, and the mixture must be separated by distillation in order to obtain a pure product.

The alkyl phosphates are subject to hydrolysis in both strongly acidic and basic solutions, but within the pH range one to ten, the hydrolysis is neither acid nor base catalyzed (20). The maximum rate of hydrolysis occurs for the singly ionized negative species, $RHPO_4^-$. Doubly ionized alkyl phosphate, $RPO_4^=$, is completely stable while the neutral species, RH_2PO_4, is relatively stable. Other workers in the field (16) report that the primary alkyl phosphates are stable in alkaline medium but are attacked in acid solution upon heating. The results are explained as a nucleophilic attack by water on the alkyl phosphates. The doubly ionized form repels the negative dipole of the water so that the reactants do not come in contact with one another. In the singly ionized form there is only a moderate repulsion between the water and the phosphorus atom. The close approach of the reactant molecules is restricted but not prevented. The negative charge on the phosphorus compound, $RHPO_4^-$, also weakens the phosphorus-oxygen link so that hydrolysis occurs with the nucleophilic attack of water on the phosphate. The bonding of the neutral compound is strong enough to hinder hydrolysis.

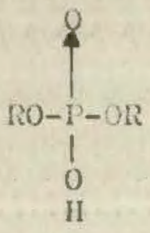
The structure of the alkyl phosphates is related to phosphoric acid. The phosphorus is the central atom with four nearly equally spaced oxygen atoms at the corners of the tetrahedra. The alkyl groups are bound to the oxygen

atoms by a covalent bond. The bond between oxygen and the hydrogen is largely ionic so that the hydrogen ion can alternate among the available oxygens. Phosphorus has five valence electrons, and by sharing electrons in a covalent bond with the oxygen of three hydroxyl or alkoxy groups, the octet for both phosphorus and oxygen is completed. The electron pair remaining on the phosphorus is shared with an oxygen atom and a semipolar or coordinate covalent bond is formed. The conclusion that this oxygen is singly bonded is supported by parachor and molecular refractivity measurements (21). The result of this semipolar bond is a partial negative charge on the semipolar bonded phosphoryl oxygen and a partial positive charge on the phosphorus. The structure is represented schematically as follows:



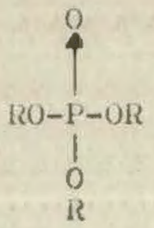
$$\mathrm{HO{-}}\underset{\substack{|\\ \mathrm{O}\\ \mathrm{H}}}{\overset{\substack{\mathrm{O}\\ \uparrow}}{\mathrm{P}}}\mathrm{{-}OR}$$

Primary ester



$$\mathrm{RO{-}}\underset{\substack{|\\ \mathrm{O}\\ \mathrm{H}}}{\overset{\substack{\mathrm{O}\\ \uparrow}}{\mathrm{P}}}\mathrm{{-}OR}$$

Secondary ester



$$\mathrm{RO{-}}\underset{\substack{|\\ \mathrm{O}\\ \mathrm{R}}}{\overset{\substack{\mathrm{O}\\ \uparrow}}{\mathrm{P}}}\mathrm{{-}OR}$$

Tertiary ester

As the acid groups of phosphoric acid are progressively esterified, both the additive property of the semipolar bonded oxygen and the acidity of the remaining acid groups on the primary or secondary esters are increased. Hydrogen bonding experiments (22) support the first state-

ment while titration experiments (23) confirm the second. The increase in additivity with substitution is correlated with the fact that the release of electrons to the phosphorus by the alkoxy group is greater than the hydroxyl group (24). The increased electron density on the phosphorus is inductively transferred to the other groups attached to the phosphorus. As a result, the negative charge on the semipolar bonded oxygen is increased, and it attracts the proton more strongly.

The increase in acidity, as phosphoric acid is esterified, is accounted for by four factors: inductive, statistical, steric, and solvation (23). The inductive effect, discussed above, tends to decrease the acid strength since the increased negative charge on the oxygens attached to the phosphorus hold the proton more firmly. The statistical factor also tends to decrease the acid strength. It depends upon the number of hydrogens which can ionize opposed to the number of negative oxygens in the anion to which the proton can return. The solvation effect is large and tends to increase the acid strength. The substituted phosphoric acid has fewer acid groups and is less solvated. The decrease in solvation energy results in an increase in the ionization constant. Steric effects depend upon the special arrangement of the molecule, and each compound is treated as an individual case. The sum of all these factors

results in an increase in acidity with an increased number of substituting alkyl groups on the phosphoric acid. This effect is regressive with increased size of the alkyl groups.

Scandium, Yttrium, Lanthanum, and the Rare Earth Elements

Radioactive isotopes of the group IIIa elements were used to study the effectiveness of the alkyl phosphoric acids as extraction reagents. A brief summary of the chemical and nuclear properties of these elements pertaining to this work follows.

Scandium, yttrium, and lanthanum (1) are all electro positive elements and contain three electrons more than the preceding inert gas. Utilization of these three electrons produces a tripositive ion with an inert gas electronic configuration. In common with other positive ions which have this configuration, there is a strong tendency to form salt-like compounds. Compounds of these elements follow the relationships established between the alkali and alkaline earth groups. For example, the hydroxides of the IIIa elements are more insoluble than the alkaline earth hydroxides, and the solubility increases from scandium to lanthanum (25). The group IIIa hydroxides are obtained as slimy precipitates upon addition of alkali hydroxides or ammonia, and they are insoluble in an excess of the reagents. Lanthanum oxide is almost as strongly basic as calcium oxide. The

ions with smaller ionic radii allow closer approach of negative ions and in accordance with Coulomb's Law are held more firmly. Thus the basicities increase and the stability of the complex compounds decreases with increasing atomic number in the series scandium, yttrium, and lanthanum.

Scandium, yttrium, and lanthanum resemble the rare earths very closely. Their outer electron configuration is essentially the same, their stable oxidation state is tripositive, and their ionic radii have the same range of values.

The rare earth elements have either of two electronic (1) configurations $4f^n5s^25p^65d6s^2$ or $4f^{n+1}5s^25p^66s^2$. The energy differences between the two configurations are small, and for chemical purposes the approximation that all the rare earth elements have the normal electronic configuration, $4f^n5d6s^2$, is satisfactory. Fourteen electrons are added to the 4f subshell as the atomic number increases from 57 to 71. These 4f electrons are not involved in the normal formation of chemical bonds, and the chemical properties are not greatly affected. The electronic configuration of the core of the ions are $4f^n5s^25p^6$, with n representing a number from 1 to 14. Thus in their normal oxidation state the three outer electrons are available for compound formation, and the ions are tripositive. The difference in the electronic configuration of the ions, like the elements, is deep within the atom and as a first approximation does not affect their

chemical properties. However, the charge on the nucleus increases as the atomic number increases, and the electrons are held more firmly. Since no new shells have been added, the radius of both the element and the ion decreases as the atomic number increases. The contraction is small for adjacent elements, but since there are 14 rare earths, the contraction over the entire series is appreciable. In fact the ionic radius of lutetium is smaller than yttrium, although yttrium has an atomic number 32 units smaller than lutetium.

It is not surprising to find that the nitrates of the group IIIa elements are very soluble. However, a number of moderately soluble double salts with alkaline earth nitrates are formed by the rare earth elements. The oxalates are obtained as white precipitates upon addition of oxalic acid to alkaline or neutral solutions of the corresponding salts. At room temperature $Sc_2(C_2O_4)_3 \cdot 9H_2O$ separates. It is the least soluble oxalate of elements in the series (26).

Radioactive isotopes of scandium, yttrium, and lanthanum (27) can be readily obtained for tracing the reactions of these elements. Scandium-46 with a half life of 85 days can be obtained 99.9 percent radiochemically pure from Oak Ridge. It decays according to the following

scheme to give titanium-46 as a stable end product.

$$Sc^{46} \longrightarrow Ti^{46} + \beta^-$$

The decay process is accompanied by emission of gamma radiation with energies of 0.885 Mev and 1.119 Mev. Yttrium-91 with a half life of 61 days can be obtained 99.9 percent radiochemically pure from Oak Ridge. It decays by beta emission (27) to zirconium-91 as a stable end product.

$$Y^{91} \longrightarrow Zr^{91} + \beta^-$$

Only 0.3 percent of the yttrium beta radioactivity is accompanied by gamma radiation. Naturally occurring lanthanum when irradiated by neutrons forms radioactive lanthanum-140. It has a half life of 40.2 hours. As the decay scheme indicates (27) the stable end product is cerium.

$$La^{140} \longrightarrow Ce^{140} + \beta^-$$

The decay is accompanied by gamma radiation with energies up to 1.60 Mev.

Solvent Extraction Theory

A brief discussion of the theory and practice of the solvent extraction process is included so that the problems involved in this work can be understood.

Solvent extraction refers to the partition of a third material between two immiscible liquid phases. In work of

this kind one of the phases is usually water, or an aqueous solution, while the other phase is an organic liquid immiscible with water.

The usefulness of any solvent pair follows from the mutual solubility of the third component in each of the solvents. The solubility of the solute depends ultimately upon the energy of solution of the pure compound. However, it is sufficient to note that compounds dissolve in chemically similar solvents (4). Water has a high dielectric constant and is composed of polar molecules. Furthermore, it can form chemical or hydrogen bonds with many ionic and polar substances forming hydrates. Thus it is not surprising that water is an excellent solvent for most inorganic salts. However, organic solvents are, in general, relatively nonpolar and un-ionized. Since there is no great similarity between the ionic salts and the usual organic solvents, the salts are insoluble in this medium (18). The reverse is true of nonpolar organic solutes. These compounds dissolve readily in the usual organic liquids because of similarity of the forces bonding the molecules but tend to be squeezed out of a water solution because of the strong attraction of the polar water molecules for one another.

The solvent extraction of a metal ion can be accomplished by finding a metal compound which is soluble in two totally different kinds of solvents. Each solvent requiring

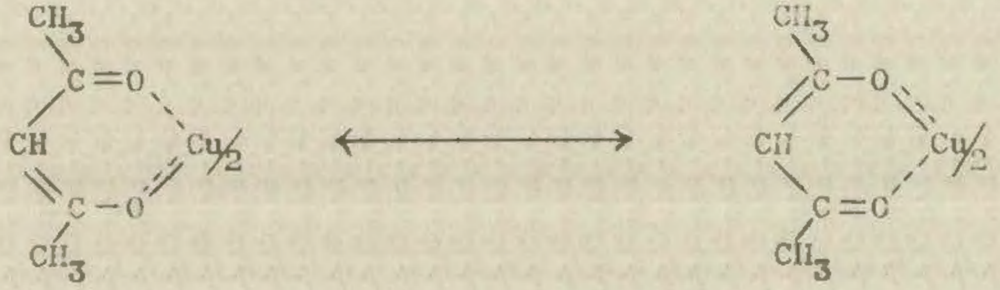
a different set of properties of the metal compound if it is to be appreciably soluble. In many cases chelate anions reversibly form neutral complexes with the cation which are soluble in the organic phase. In their ionized form the compounds are, of course, soluble in aqueous solutions. Examples of this are complexes of metal ions (2, 18) involving oxine, dithizone, cupferron, and thenoyltrifluroacetone.

The formation of an extractable neutral compound is a vital step in the liquid-liquid extraction process, and so the factors governing the type of compound have an important bearing on the reaction. Compounds are classified according to the nature of the bonding between the metal ion and the anion. This may be either electrostatic or covalent although most compounds are intermediate between these two extremes. Anions which are easily polarized readily form covalent bonds. Small highly charged cations encourage polarization of the anion so that covalent bonding is most probable between small cations and easily distorted anions (5). Ionic bonding predominates between large univalent cations and the less easily distorted anions. For example, the iodide ion is large and easily polarized while the fluoride ion is considerably smaller and is not easily distorted. Magnesium forms a small highly charged cation so that magnesium iodide has considerable covalent character. Cesium has a low charge density so that the bonding in cesium fluoride is largely ionic.

The strength of the bonds of a covalent compound is dependent upon the acidity of the metal ion, basicity of the anion, steric factors, and availability of electron orbitals on the cation (18). There are many cases where very stable complexes are formed by the sharing of a sufficient number of electron pairs between the cation and anion so that the total number of electrons in the valence shell of the cation approaches the number of electrons in the outer shell of the next inert gas. There are stable configurations for the outer electrons other than the inert gas configuration, however, the important point is that there are certain restrictions on the arrangement of the electrons about the cation. Of course, there may not be enough space about the cation to fit all anions required for neutralization of the charge or to satisfy the coordination number of the metal ion. In this event one of the covalent bonds is weakened or nonexistent. The strength of the covalent bond increases with the acidity of the cation and basicity of the anion. The acidity of the cation can be correlated roughly with charge density, small highly charged metal ions being the most acidic. The basicity which the anion exhibits for a metal ion does not necessarily correspond to the basicity exhibited for a proton. Steric limitations account for part of the difference in basicities since there is considerable difference in the size of the proton and metal ions.

The stability of chelate complexes depend in part upon the same factors which govern the stability of simple complexes and in part upon factors which are characteristic of the chelate compounds. The name, chelate, applies to a class of compounds having more than one functional group per molecule stericly placed so that more than one group per molecule can react with the cation. The reactive groups of the chelate may be either neutral or negative, but they are always basic. The negative groups, of course, arise from ionization of a parent acid. The functional groups in a molecule do not need to be alike, although this may occur. However, the groups must be stericly placed in the chelate compound so that more than one functional group can react with the metal without introducing strains in the molecule. Five or six member rings are usually established in the chelate metal complex since this configuration is free from strain (2). If the functional groups of the chelate are separated by too great or too small distances, the complex will not form because the bonds of the compound under strain and the energy of chelation is offset by the energy required to introduce the strain. There are a few chelate complexes which have four membered rings, and in some cases these may be quite stable. Some chelate compounds form a number of rings with the metal ion. The relationship between the number of rings and the stability of the complex is an

interesting one. As the number of rings increases, the stability of the complex increases (2). This follows from the reaction which occurs when the complex is formed. When the complex with the larger number of rings is formed, a greater number of water molecules is released. This means that the total number of particles produced in the reaction is larger. This is called the entropy effect and results in increased stability. Resonance also contributes to the chelate complex stability (2). The stability of the copper chelates of β-diketones is attributed to resonance.



Another example of resonance stabilization is the iron II and iron III chelates of orthophenanthroline.

The factors governing solvent extraction of metal ions by organic complexing agents (28) are best understood by considering the following over-all reaction.

$$M^{+n}_{(w)} + nHQ_{(o)} \longrightarrow MQ_{n(o)} + n'H^{+}_{(w)} \qquad \text{Eq. 1}$$

where M^{+n} = metal ion of oxidation number n,
HQ = organic acid,
MQ_n = metal complex,
(w) = water phase,
(o) = organic phase,
n = n' (to be defined later)

The equilibrium constant, K_M, of the reaction is given by Equations 2 and 3.

$$K_M = \frac{\left[MQ_n\right]_{(o)} \left[H^+\right]^{n'}_{(w)}}{\left[M^{+n}\right]_{(w)} \left[HQ\right]^{n}_{(o)}} \qquad \text{Eq. 2}$$

$$K_M = D_M \times \frac{\left[H^+\right]^{n'}_{(w)}}{\left[HQ\right]^{n}_{(o)}} \qquad \text{Eq. 3}$$

where

$$D_M = \frac{\left[MQ_n\right]_{(o)}}{\left[M^{+n}\right]_{(w)}}$$

The over-all equation is a simplified expression (2) which is derived from the following independent reactions:

$$HQ_{(o)} \longrightarrow HQ_{(w)} \qquad \text{Eq. 4}$$

$$HQ_{(w)} \longrightarrow Q^-_{(w)} + H^+_{(w)} \qquad \text{Eq. 5}$$

$$M^{+n}_{(w)} + nQ^-_{(w)} \longrightarrow MQ_{n(w)} \qquad \text{Eq. 6}$$

$$MQ_{n(w)} \longrightarrow MQ_{n(o)} \qquad \text{Eq. 7}$$

When the concentration of the metal complex, MQ_n, in the water phase is much smaller than the total concentration of

the metal in the water phase, the over-all equation and the equilibrium constant are good approximations.

The structure of the organic acid can have opposing effects on the over-all distribution of the metal ion between the phases. For example, changes in the structure of the complexing reagent which increases the solubility of the metal complex in the organic phase also decreases the concentration of the complexing reagent in the water phase. Thus, while Equation 7 is driven further to the right, Equations 4, 5, and 6 are displaced to the left, and the over-all effect may drive Equation 1 in either direction.

Separation of metal ions by solvent extraction depends upon differences in the values of K_M for the metals. For equal acid concentrations, reagent concentrations and similar structures of the metal complex, the tendency to enter the organic phase is proportional to the equilibrium constant. If the proper reagent and acid concentrations are chosen, one metal preferentially enters the organic phase, and the other metal remains in the water phase. The greater the difference in K_M, the better the separation.

Equation 3 can be rearranged for convenience to Equation 8.

$$\mathrm{Log}K_M = \mathrm{Log}D_M + n'\mathrm{Log}\left[H^+\right]_{(w)} - n\mathrm{Log}\left[HQ\right]_{(o)} \qquad \text{Eq. 8}$$

When the acid concentration is constant, a straight line equation results.

$$\text{LogD}_M = n\text{Log}\left[HQ\right]_{(o)} + b \qquad \text{Eq. 9}$$

where $b = \text{LogK}_M - n'\text{Log}\left[H^+\right]_{(w)}$

and $\left[H^+\right]$ = a constant

Equations similar in form to Equation 9 are used in the study of the over-all reaction which occurs in solvent extraction. For example, n of Equation 9 is defined by Equation 10. It is obtained by differentiating Equation 8 or 9 at constant acid concentration.

$$n = \frac{\partial\ \text{LogD}_M}{\partial\ \text{Log}\left[HQ\right]_{(o)}}, \quad \left[H^+\right]_{(w)} = \text{const.} \qquad \text{Eq. 10}$$

The slope, n, defined by Equation 10 is the coefficient of HQ. Differentiation of Equation 8 at constant reagent concentration gives Equation 11.

$$n' = \frac{\partial\ \text{LogD}_M}{\partial\ \text{Log}\left[H^+\right]_{(w)}}, \quad \left[HQ\right]_{(o)} = \text{const.} \qquad \text{Eq. 11}$$

The slope, n, defined by Equation 11 is the coefficient of H^+ in the over-all reaction. In the special case studied here, the two coefficients, n and n', are the same, but this may not be true for other cases. In practice, the metal distribution coefficients versus the appropriate term of Equation 1 are plotted on log-log graph paper, and the slopes are determined from the graph.

The reagent and acid concentrations at 50 percent extraction are a convenient measure of the properties of a solvent extraction system. At 50 percent extraction the metal distribution coefficient is one, and log D_M is zero; therefore, Equation 8 reduces to Equation 12.

$$\text{Log}K_M = n\text{Log}\left[H^+\right]_{(w)} - n\text{Log}\left[HQ\right]_{(o)}, \quad D_M = 1 \qquad \text{Eq. 12}$$

At an arbitrary acid concentration the reagent concentration is a measure of the metal equilibrium constant as Equation 13 indicates.

$$\text{Log } HQ_{(o)} = \frac{1}{N} \cdot pK_M + C, \qquad D_M = 1 \qquad \text{Eq. 13}$$

where $pK_M = -\text{Log}K_M$

C = const. (the pH is held constant.)

Radiochemistry of Solvent Extraction

Radioactive tracers can be used to follow the reaction occurring in a solvent extraction system. The radioactivity of the tracer is measured and is related to the concentration of the isotope by an unknown constant. However, if the measurement of the radioactivity is carried out under carefully controlled conditions, this constant will remain the same throughout the series of experiments. Ratios of radioactivity in a unit volume then become ratios of concentrations.

The radioactive isotope used to trace a reaction differs from inactive isotopes only in nuclear properties and atomic weight. The chemical properties of the isotopes of the lighter elements and their compounds exhibit slight differences due to atomic mass effects. This isotopic effect becomes negligible with the increasing atomic weight. For solvent extraction studies the chemical reactions of all isotopes of an element are considered equivalent.

III. EXPERIMENTAL

Preparation of Alkyl Phosphates

Both classical methods described in the discussion were used to prepare the alkyl phosphates (16). However, the reaction between alcohol and phosphorus pentoxide was used to

prepare only the methyl phosphoric acids. The products of the reaction, dimethyl- and monomethyl phosphoric acid, were separated by precipitation of the barium salt of monomethyl phosphoric acid. The acid of the secondary ester was recovered by double decomposition of the barium salt with sulfuric acid. Since diethyl phosphoric acid boils at 117°C. under a pressure of 0.01 millimeters (29), the dimethyl phosphoric acid was distilled at reduced pressure.

Preparation and purification of dimethyl phosphoric acid. Ninety-six grams of absolute methyl alcohol was added to the suspension of 142 grams of phosphorus pentoxide in carbon tetrachloride. The reaction proceeded according to the following equation:

$$3CH_3OH + P_2O_5 \longrightarrow (CH_3O)(HO)_2PO + (CH_3O)_2(HO)PO$$

After the reaction was completed as indicated by solution of the phosphorus pentoxide, 200 milliliters of water was added, and the mixture was neutralized with a boiling solution containing barium hydroxide to pH 10. The precipitate of monomethyl barium phosphate was filtered from the solution. A two percent excess, 50 grams, of concentrated sulfuric acid was added to the solution containing dimethyl barium phosphate, and the barium sulfate was removed. The filtrate, a solution of dimethyl phosphoric acid, was allowed to evaporate at room temperature. The dimethyl phosphoric acid was

then distilled under a pressure of less than one millimeter. The temperature of the material in the distillation flask during the distillation was 190° to 225°C. The distillate had a temperature of 113° to 118°C. at the head of the fractionating column. The density of successive fractions in this temperature range of the distillate were 1.323, 1.316, and 1.320 grams per milliliter. The product of the distillation possessed no acid properties, but after standing 15 hours in water, 0.661 grams of the product neutralized 4.62 milliequivalents of standardized base.

Part of the product of the distillation of dimethyl orthophosphoric acid appears to have been tetramethyl pyrophosphate.

$$2(CH_3)_2HPO_4 \longrightarrow (CH_3)_4P_2O_7 + H_2O$$

The product of the distillation was neutral which is in accord with the structure of tetramethyl pyrophosphate. Upon standing in a water solution the pyro form was hydrolyzed to the ortho form, and the solution became acidic. Only one

$$(CH_3)_4P_2O_7 + H_2O \longrightarrow 2(CH_3)_2HPO_4$$

inflection point was observed in the pH-neutralization curve which indicated only one acid group per phosphorus atom. This is in accord with the structure of dimethyl orthophosphoric acid. Tetramethyl pyrophosphate has been reported to thermally decompose to trimethyl orthophosphate (29).

This compound is neutral and resists hydrolysis. Its presence in the tetramethyl pyrophosphate is detected by the apparent increase in the formula weight of the tetramethyl pyrophosphoric acid as determined by the hydrolysis and titration experiments. The trimethyl orthophosphate has a lower density than the tetramethyl pyrophosphate, and its presence as a contaminate in the tetramethyl pyrophosphate results in a decreased density. The observed density is less than the reported density of the tetramethyl pyrophosphate. Calculation of the composition of the distillate from titration and density measurements indicates the following composition: by titration measurements, 82 percent by weight of tetramethyl pyrophosphate; and by density measurements, 77 percent by weight of tetramethyl pyrophosphate. In view of the indeterminate results obtained with this preparation, it was decided to use another method for preparing the alkyl phosphates.

The alkyl dichlorophosphates can be intermediates in the preparation of the monoalkyl phosphoric acids. They are prepared according to the following equation:

$$ROH + POCl_3 \longrightarrow (ROH)Cl_2PO + HCl$$

The preparation of monoalkyl dichlorophosphate. One and a half moles of phosphorus oxychloride was placed in a one liter, three-necked flask. A dropping funnel, which was fitted with a stopcock and filled with one mole of the alcohol,

a reflux condenser, and a thermometer were connected to the flask. After the flask and contents were cooled in an ice bath, the alcohol was added at a rate of one mole in fifteen minutes. The mixture was stirred vigorously with a teflon coated magnetic stirring bar during the alcohol addition. A water aspirator was connected to the reflux condenser shortly after the reaction was started. After the alcohol was added, the product was allowed to come to room temperature under reduced pressure and with vigorous stirring.

The purification of the alkyl dichlorophosphates. The alkyl dichlorophosphates were isolated by fractional distillation at a pressure of less than one millimeter. The apparatus for the distillation consisted of a one liter distilling flask, an air-cooled fractionating column (1 X 12 inches), a water-cooled condenser, and a multiple fraction selector. The multiple fraction selector allowed four fractions of the distillate to be taken without breaking the vacuum. Phosphorus oxychloride and the alkyl dichlorophosphate were collected in the distillate while the dialkyl chlorophosphate remained in the distilling flask. The temperature of the alkyl dichlorophosphate vapor at the fractionating column head is given by Table I. The density of the distillate was compared to the estimated density of these compounds as a rapid check on the purity of the various fractions collected.

TABLE I

PHYSICAL PROPERTIES OF THE ALKYL CHLOROPHOSPHATES

Compound*	Temp. of vapor (degrees C.)	Experimental density 24°C. (gm/ml)	Calculated density 24°C. (gm/ml)	Reported density(16) 24°C. (gm/ml)
$POCl_3$	30			1.671
$(EtO)Cl_2PO$	44-49	1.375	1.377	1.348
$(PrO)Cl_2PO$	44-48	1.317	1.307	
$(BuO)Cl_2PO$	59-61	1.252	1.252	1.257
$(AmO)Cl_2PO$	62-67	1.210	1.212	
$(HexO)Cl_2PO$	70-75	1.182	1.178	
$(OctO)Cl_2PO$	91-100	1.127	1.125	

*The symbols are defined as follows: Et, ethyl; Pr, n-propyl; Bu, n-butyl; Am, n-amyl; Hex, n-hexyl; and Oct, n-octyl.

The distillation apparatus described above did not give a satisfactory separation for derivatives with less than three carbon atoms. The boiling points of these derivatives were sufficiently close to that of phosphorus oxychloride that efficient separations with the available equipment was impossible. For these derivatives the phosphorus oxychloride was eliminated after the first distillation by hydrolysis to phosphoric acid with ice water. The immiscible water phase was removed with a separatory funnel, and the alkyl chlorophosphate was redistilled under a pressure of

less than one milliliter. The density of the propyl dichlorophosphate was reduced from 1.349 to 1.317 grams/milliliter by this procedure. The alkyl dichlorophosphate is less reactive than phosphorus oxychloride and is not hydrolyzed rapidly at 0°C.

Hydrolysis of the alkyl chlorophosphates. A precipitate of the barium monoalkyl phosphate was obtained from the alkyl dichlorophosphate in two steps as the equations indicate:

$$RCl_2PO_2 + 2NaOH \xrightarrow{95^\circ} RH_2PO_4 + 2NaCl$$

$$RH_2PO_4 + BaCl_2 + 2NaOH \xrightarrow{95^\circ} RBaPO_4 + 2NaCl$$

The chlorosphosphate (0.55 mole) was placed in a four liter beaker and about 500 milliliters of water was added. The mixture was heated to 95°C., and a concentrated solution containing 1.1 moles of sodium hydroxide was added very slowly and stirred vigorously. The reaction was sometimes slow to start. Because of this induction period only a small amount of sodium hydroxide was added at the beginning of the reaction. After the reaction started, as indicated by vigorous boiling, it was no longer necessary to heat the mixture. The barium chloride (0.55 mole) and 0.25 mole of ammonium chloride were dissolved in the solution containing the alkyl phosphoric acid, and the volume was diluted to one and a half liters. While the solution was stirred vigorously, a concentrated

solution containing 1.1 moles of sodium hydroxide was added slowly. The mixture containing the precipitated barium alkyl phosphate was filtered. The precipitate was washed with water eight times, and washed with acetone two times. The barium alkyl phosphate was air-dried 12 hours, heated at 110°C. for 30 minutes, and then dried over silica gel for several days. Small samples gave no further weight loss when heated in the oven at 110°C. The yield of the reaction was based on the formula weight of the barium monoalkyl phosphate and was essentially 100 percent of the theoretical yield.

The monoalkyl phosphoric acid was obtained by double decomposition of the corresponding barium salt with sulfuric acid. A two percent excess of sulfuric acid (0.56 mole) was added to 0.55 mole of barium monoalkyl phosphate.

$$RBaPO_4 + H_2SO_4 \longrightarrow RH_2PO_4 + BaSO_4$$

The concentrated sulfuric acid was dissolved in 100 milliliters of water. This was added to the barium monoalkyl phosphate. The mixture containing barium sulfate and monoalkyl phosphoric acid was thoroughly stirred and allowed to stand 12 hours. The alkyl phosphoric acid was extracted from the mixture by the following procedure: The mixture containing barium sulfate and alkyl phospheric acid was centrifuged, and the solution containing the alkyl phosphoric acid was

decanted from the precipitated barium sulfate. Fifty milliliters of water was added to the barium sulfate, and it was thoroughly stirred, centrifuged, and the solution decanted. The procedure was repeated four times. This procedure kept the volume of monoalkyl phosphoric acid solution as small as possible, and it eliminated filtration. The latter operation was virtually impossible because the alkyl phosphoric acid aided suspension and dispersion of the barium sulfate. The above extraction procedure was modified for the octyl derivative since it was not soluble in water. The suspension containing barium sulfate and octyl phosphoric acid was extracted five times with fifty milliliter portions of ether.

With the exception of the octyl derivative the 250 milliliter aqueous solution containing monoalkyl phosphoric acid and a small amount of sulfuric acid was extracted five times with 100 milliliter portions of ether in a separatory funnel. The recovery of the alkyl phosphoric acid from its aqueous solution into ether with one extraction and five extractions is indicated by Table II.

TABLE II

RECOVERY OF MONOALKYL PHOSPHORIC ACID BY ETHER EXTRACTION*

Compound	Material recovered in ether with one extraction	Material recovered in ether with five extractions
PrH_2PO_4	4%	13%
BuH_2PO_4	12%	47%
AmH_2PO_4	28%	81%
$HexH_2PO_4$	68%	99.5%

*250 milliliters of aqueous alkyl phosphate were extracted with 100 milliliters of ether the indicated number of times.

The combined ether solution containing each compound was washed twice with ten milliliters of water in order to remove the last trace of sulfuric acid.

The ether solutions were evaporated at room temperature, and the residues containing monoalkyl phosphoric acid were dried over silica gel for several weeks. Part of the monoalkyl phosphoric acid was cooled with liquid nitrogen and then allowed to return to a temperature a few degrees lower than its melting point. The seed crystals obtained soon converted the viscous liquid to a crystalline solid. The freshly prepared crystalline material had a faint greenish tinge. However, at room temperature this color quickly changed to pale amber. The presence of either dialkyl pyrophosphoric acid or water lowered the melting point of monoalkyl orthophosphoric acid. The butyl

derivative was recrystallized from a solution containing about 70 percent hexane and 30 percent chloroform. A slightly cloudy solution was obtained by adding hexane to a chloroform solution of the butyl phosphoric acid. A few drops of chloroform clarified the solution. The solution was cooled to -20°C., seeded, and allowed to stand 15 hours. The mother liquor was decanted and the crystals dried under reduced pressure. The other compounds could not be recrystallized by this method. The melting points of the crystalline monoalkyl phosphoric acids are given in Table XII.

The Structure and Analysis of the Monoalkyl Phosphoric Acids

A weighed amount of the solid monoalkyl phosphoric acid was titrated with 0.1 normal sodium hydroxide. The pH was determined with a model G Beckman pH meter equipped with glass and calomel electrodes. A plot of pH versus the number of equivalents of base added to the alkyl phosphoric acid had inflection points for all the water soluble derivatives at a pH 4.5 and 9.5. About 20 percent acetone was added to solutions of the octyl phosphoric acid, and as a result the inflection points were displaced to higher pH values. For aged samples of the monoalkyl phosphoric acid, the second end point required twice as many equivalents of standard sodium hydroxide as the first end point. These two experimentally determined equivalent weights of the acid corresponded to one formula weight of the monoalkyl phosphoric acid. These

data indicated no less than two acid groups per molecule. Results of the titration of the monoalkyl orthophosphoric acids are given in Table III.

TABLE III

FORMULA WEIGHT FROM POTENTIOMETRIC TITRATIONS*

Compound	Experimental formula weight	Calculated formula weight
BuH_2PO_4	154	154
AmH_2PO_4	173	168
$HexH_2PO_4$	188	182
$OctH_2PO_4$	210	210

*$\frac{\text{Weight of sample}}{\text{equivalents of base}}$ = formula weight

When neutral barium chloride was added to the sodium alkyl phosphate at a pH 9.5, no change in pH was observed. This indicated no more than two acid groups per formula weight.

The solid monoalkyl phosphoric acid was analyzed for phosphorus. The organic portion of the molecule was destroyed by fuming with concentrated nitric acid. Both sulfuric acid and perchloric acid interfered with the phosphorus determination of standard samples and could not be used to destroy the organic matter. The sample was placed in a 400 milliliter beaker. About 20 milliliters of red fuming nitric acid was added and evaporated to dryness on a hot plate. Two milliliters of concentrated nitric acid was

added and then evaporated to dryness. The addition of two milliliters of acid was repeated a total of 15 times or five times after the last trace of charred material disappeared. It was necessary to control the fuming process closely to prevent volatilization of the phosphoric acid as metaphosphoric acid. The phosphoric acid was precipitated as magnesium ammonium phosphate according to the procedure recommended by Kolthoff and Sandell (30). Magnesium ammonium phosphate hexahydrate was the form weighed. It was washed with alcohol and ether and then air-dried. The average of the duplicate analyses is given in Table IV.

TABLE IV

ANALYSIS OF MONOALKYL PHOSPHORIC ACIDS

Compound	Experimental phosphorus content	Theoretical phosphorus content
PrH_2PO_4	22.2%	22.11%
BuH_2PO_4	20.0%	20.11%
AmH_2PO_4	18.3%	18.44%
$HexH_2PO_4$	16.9%	17.01%
$OctH_2PO_4$	14.5%	14.75%

The alkyl pyrophosphoric acids. When the monoalkyl phosphoric acids were heated for 12 hours at 115°C.[1] in an

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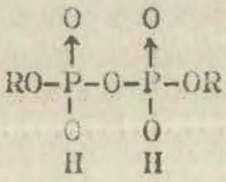
[1] This was the setting of the oven and since there was no logical basis for a choice of a temperature this value was used.

open vessel, the titration curves were different from the titration curves of the original material. The equivalents of base required to neutralize one gram of acid between pH 4.5 and 9.5 decreased by as much as 10 percent. Since orthophosphoric acid is known to form pyrophosphoric acid when it is heated, it is assumed that in this case a pyrophosphate was formed. The dialkyl pyrophosphoric acid has only one acid group per phosphorus atom. This is in accord with the experimental fact that an appreciable fraction of the phosphoric acid in the heated mixture had only one acid group per phosphorus atom.

$$2RH_2PO_4 \xrightarrow[12\ \text{hours}]{115^\circ} R_2H_2P_2O_7 + H_2O$$

The probable structure of the dialkyl pyrophosphoric acid resembles the structure of pyrophosphoric acid.



$$\begin{array}{c} \quad\ \ O \quad\ O \\ \quad\ \ \uparrow \quad\ \uparrow \\ RO-P-O-P-OR \\ \quad\ \ | \quad\ \ | \\ \quad\ \ O \quad\ O \\ \quad\ \ H \quad\ H \end{array}$$

Dialkyl Pyrophosphoric Acid

The percent of phosphorus atoms in the form of dialkyl pyrophosphoric acid after the sample was heated for 12 hours at 115°C. in an open vessel is given in Table V. However, the composition remains the same if the samples are heated for longer periods.

TABLE V

THE COMPOSITION OF THE HEATED* MONOALKYL PHOSPHORIC ACIDS

Compound	Ortho acid	Pyro acid
BuH_2PO_4	91%	9%
AmH_2PO_4	93%	7%
$HexH_2PO_4$	95%	5%
$OctH_2PO_4$	90%	10%

*The samples were heated at 115°C. for 12 hours in an open vessel.

When the dialky pyrophosphoric acid was formed, water was given off and the weight decreased. The actual loss in weight when the sample was heated was somewhat variable because the phosphate esters were very hygroscopic and traces of water were almost always present. However, when the average values of the loss in weight were used for samples which had been thoroughly dried, they supported the data of Table V which are based on titration experiments.

The hydrolysis of the alkyl pyrophosphoric acids. Samples of the alkyl phosphoric acid which contained as much as 10 percent of the pyro form were sealed in a tube with a large excess of water. The tube was heated 12 hours on a steam bath. The equivalents of base required to neutralize one gram of acid at pH 4.5 remained the same as in the two previous titrations. However, the equivalents of base

required to neutralize one gram of acid from pH 4.5 to 9.5 increased, above the value for the reagent containing 10 percent pyro form, to the original value for the untreated reagent. This indicated hydrolysis of the pyro form to the ortho form.

$$R_2H_2P_2O_7 + H_2O \xrightarrow[12 \text{ hours}]{100°C.} 2RH_2PO_4$$

The alkyl orthophosphoric acids prepared according to the procedure used in this work were contaminated by the corresponding pyrophosphoric acids. Traces of the pyrophosphoric acids persisted in water solutions at room temperature for as long as six months. This conclusion was supported by the high distribution coefficients obtained for the group IIIa ions and the slopes, $\frac{\partial \text{ LogD}_M}{\partial \text{ Log}\left[RH_2PO_4\right]_{(o)}}$, of the log-log plots. Both of these values were significantly different for the pyro and ortho forms. The trace of pyrophosphoric acid remaining after six months was too small to be detected by titration experiments.

Distribution Procedures

The distribution of the monoalkyl phosphoric acids was studied between the system amyl alcohol and water, and the system ether and water. A separatory funnel was used in the study of dilute solutions because large volumes were required for analysis and the phases separated rapidly. The organic

solvent, water, and alkyl phosphate were placed in the separatory funnel and stirred vigorously for ten minutes. A measured volume containing about one milliequivalent was taken from each phase for analysis. The phases containing high concentrations of alkyl phosphoric acid did not separate readily, and these were equilibrated in a centrifuge tube equipped with a glass cap. Four milliliters of organic solvent, four milliliters of water, and the alkyl phosphoric acid were placed in the tube and shaken for five minutes (see Apparatus for shaker description). The samples were then centrifuged for two minutes to two hours. The octyl phosphoric acid and amyl alcohol formed rather stable emulsions in water, and these samples were allowed to stand as long as five or six weeks. A measured volume of each phase containing about one milliequivalent was taken from the tube for analysis. The organic phases were diluted with 20 percent acetone solutions to assure one phase for titration purposes. The samples were titrated to the first end point which was 4.5 for the aqueous solutions and somewhat higher for the solutions containing acetone. The results are given in Tables VII and VIII.

The distribution of both nitric acid and the monoalkyl phosphoric acid was studied between amyl alcohol and water. Four milliliters of aqueous nitric acid, four milliliters of amyl alcohol, and one of the monoalkyl phosphoric acids were

placed in tubes and shaken for five minutes at 26±1°C. The samples were centrifuged for two minutes and measured volumes taken for analysis. The organic phase was diluted with 20 percent acetone and 80 percent water to obtain one phase for titration. Both nitric acid and half of the total alkyl phosphoric acid were neutralized at the first end point. The second acid group of the alkyl phosphoric acid was titrated between the first and second end points. The results are given in Table IX.

The distribution of the group IIIa ions in a system containing water, amyl alcohol, nitric acid, and one of the monoalkyl phosphoric acids was studied. A sample was prepared by adding the following reagents to a ten milliliter centrifuge tube: two milliliters of standardized aqueous nitric acid solution, two milliliters of amyl alcohol saturated with water, a weighed amount of one of the alkyl phosphoric acids, and usually five but sometimes ten lambda of a stock solution containing one of the radioactive group IIIa nitrates. The tube was sealed and shaken for five minutes at 26±1°C. in a constant temperature air bath. The tubes were centrifuged for two minutes and one milliliter of each phase taken for radiochemical analysis. Preparation of the various stock solutions is described under Reagents.

Scandium-46 and lanthanum-140 are gamma emitters, and the activity of the sample was determined by counting gamma

radiation. The sample was placed in an 1.8X25 centimeter test tube and diluted to a calibrated mark (about 13 milliliters) with a solution of 75 percent acetone and 25 percent water. The height of the mark on the test tube corresponded to the diameter of the photo tube of the gamma counter. The same test tube was used for counting both the amyl alcohol phase and the water phase of each distribution experiment so that it was unnecessary to calibrate the test tubes. Since 0.3 percent of the disintegrations of yttrium-91 are accompanied by gamma radiation, this method may also be used for very active yttrium samples. In a few cases yttrium-91 gamma radiation was counted, and the same results were obtained as with the procedure outlined below.

Yttrium 91 is a beta emitter, and the activity of the sample was determined by counting beta particles. The sample was placed in a small beaker. Five milliliters of yttrium oxalate stock solution (defined under Reagents) was added. The solution was slowly neutralized with concentrated ammonium hydroxide to the bromothymol blue end point and then allowed to digest at room temperature. Five minutes is sufficient for digestion, but the filtrations are much faster if the samples are allowed to digest over night at this point. The form of yttrium oxalate precipitated at room temperature is (25) $Y_2(C_2O_4)_3 \cdot 9H_2O$. Twenty-five milliliters of 95 percent ethyl alcohol was added and the sample filtered with

2.5 centimeter, number 42 Whatman filter paper. The precipitate and filter paper were washed with absolute alcohol and ether and then air-dried for ten minutes. The filter paper and precipitate were scotch taped to a small cardboard rectangle for counting.

Recovery of inactive yttrium oxalate from standardized stock solutions was studied. When the precipitated yttrium was filtered without adding alcohol, only 75 weight percent of the yttrium was recovered. When the precipitate was washed with water or ammonium oxalate, even lower recoveries were obtained. When a large excess of alcohol was used, ammonium chloride precipitated, and the weight of the product was 270 weight percent of the calculated weight.

The internal absorption of beta particles by the yttrium oxalate was not determined since the same weight of the carrier was used each time, and the fraction of the beta particles absorbed was constant.

Reagents and Standard Solutions

In general analytical grade chemicals were used in this work. The reagents used to prepare the alkyl phosphoric acids were Eastman White Label butyl alcohol, amyl alcohol, and octyl alcohol; Eastman Yellow Label hexyl alcohol; and Baker and Adamson Reagent Grade phosphorus oxychloride. Reagents used in solvent extraction work were double distilled

water, Eastman Yellow Label amyl alcohol which was distilled from a solution containing sodium pentoxide, $NaOC_5H_9$, and Baker and Adamson Reagent Grade nitric acid.

Carbonate free solutions of sodium hydroxide were prepared according to Kolthoff and Sandell (30) and standardized according to recommendations of the National Bureau of Standards[1] using potassium acid phthalate. The approximately 0.1 normal sodium hydroxide solution was placed in pint containers of polyethylene, and one sample from each of the fifteen batches was standardized. The caps were tightened and wrapped with Scotch electrical tape and stored until used.

Stock solutions of inactive yttrium used in the analysis of radioactive yttrium were prepared by dissolving one gram of yttrium oxide in 250 milliliters of concentrated hydrochloric acid, to this was added 2.1 grams of oxalic acid dihydrate, and the mixture was diluted with water to 500 milliliters.

Radioactive scandium and yttrium were obtained from Oak Ridge in 99.9 percent radiochemical purity and high specific activity. Both were obtained in a solution containing

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[1] The recommended procedure for standardizing sodium hydroxide is attached to bottles of potassium acid phthalate obtained from the National Bureau of Standards.

hydrochloric acid and some organic matter. The solutions were evaporated to dryness with an infra-red lamp in a hood. The samples were twice fumed to dryness from a solution containing concentrated nitric acid and then dissolved in a 1.25 molar nitric acid solution for use in solvent extraction work. Solutions of about 10,000 counts per minute per five lambda of standard solution were used.

Spectroscopically pure lanthanum oxide from Lindsay Light and Chemical Co. was irradiated with slow neutrons by the Los Alamos Scientific Laboratory. Two and a half milligrams of the oxide was irradiated for eight hours at a flux of 10^{10} neutrons. The sample was dissolved in ten milliliters of 1.25 molar nitric acid.

The half lives of the radioactive tracers were determined and compared to their reported half lives (27). They are as follows: lanthanum-140, 42 hours determined, 40 hours reported; yttrium-91, 60 days determined, 57 days reported; scandium-46, 82 days determined, 85 days reported.

Apparatus

A mechanical shaker was used to equilibrate the liquid-liquid extraction samples. It shook the samples 120 times a minute at 26±1°C. in an air bath equipped with a thermoregulator. The samples were shaken for five minutes. However, the time that the samples were shaken was not critical because the samples shaken for two to ten minutes gave the

same results.

Centrifuge tubes were used to equilibrate the liquid-liquid extraction extraction samples. These held about ten milliliters and were 1.8 X 10 centimeters. They were fitted with standard taper caps. Five tubes could be accommodated by the shaker at one time. The tubes were held in place in the shaker by spring clamps.

The counting equipment for gamma-radiation consisted of a scintillation crystal, photo multiplier, amplification circuits, binary scaler, and mechanical register. The electronic circuits were prepared by the electronic section of the Los Alamos Scientific Laboratory.

The counting equipment for beta-particles consisted of an end window geiger tube, a commercial unit for amplification and counting, and a mechanical register.

IV. CALCULATIONS

Density Calculations

The calculated densities of the alkyl dichlorophosphates were based on reported densities (16) of phosphorus oxyclhoride and the trialkyl phosphate. A weighted average of the molar volumes of these compounds gave an estimated molar volume for the alkyl dichlorophosphate. The estimated molar volume and the formula weight were used

to calculate the densities of the alkyl dichlorophosphates. As an example, the calculation of butyl dichlorophosphate is shown.

Compound	Reported density 24°C.	Molecular weight	Molar volume
$(BuO)_3PO$	0.9735 gm/ml	266.3 gm/mole	$\frac{266.3}{0.9735}$ = 273.5 ml/mole
$POCl_3$	1.671 gm/ml	153.4 gm/mole	$\frac{153.4}{1.671}$ = 92.0 ml/mole

1/3 x molar volume of $(BuO)_3PO$ + 2/3 x molar volume of $POCl_3$ = molar volume of $(BuO)Cl_2PO$

1/3 x 273.5 + 2/3 x 92.0 = 152.5 ml

density = molecular weight/molar volume

d = 191.0/152.5 = 1.252 gm/ml density of $(BuO)Cl_2PO$

In several cases the density of the trialkyl phosphate was not reported at 24°C. Linear extrapolations from the values reported to 24°C. were used in these cases. Also there were no reported densities for trihexyl phosphate and trioctyl phosphate. From the linear increase of the molar volume with the length of the carbon chain, it was concluded that each additional methylene group added 16.8 milliliters to the molar volume of the alkyl phosphates. This value was used to estimate the molar volume of hexyl dichlorophosphate and octyl dichlorophosphate.

The calculated densities of the alkyl phosphoric

acids were handled in the same way as above. The basis for the calculations was the reported densities of the trialkyl phosphates and orthophosphoric acid. A weighted average of the molar volumes of the above compounds gave an estimated molar volume for the alkyl phosphoric acid. The formula weight divided by the estimated molar volume gave the calculated density.

The monoalkyl phosphoric acids are very viscous, and therefore, their densities were not observed. However, the densities of solutions of known concentrations were obtained. These solutions were prepared from a known volume and weight of amyl alcohol and a known weight of monoalkyl phosphoric acid. The density of the solution determined the total volume. The volume of the solvent was subtracted from the total volume, and the volume of the monoalkyl phosphoric acid was obtained. From the volume and the weight, the density of the monoalkyl phosphoric acid was calculated. The reciprocal of the density is the specific volume. It is used in the next section to convert concentration units from a weight basis to a molar basis.

Determination of the Alkyl Phosphoric Acid and Nitric Acid Concentrations

The nitric acid concentration of the water phase in the metal distribution experiments was calculated from the amount of nitric acid used and the distribution indicated by

Table IX. It was assumed that the volume of the aqueous nitric acid solution and the saturated amyl alcohol stock solutions did not change when the samples were equilibrated. About two percent of the amyl alcohol left the organic phase and entered the water phase while a small amount of the nitric acid left the water and entered the amyl alcohol. Since water is appreciably soluble in amyl alcohol, it was saturated before use in order to minimize volume changes. The actual volumes after equilibrium were within two percent of the original volumes. Since the precision of the determination of the metal distribution coefficients was about six percent, the calculated concentration of nitric acid was sufficient.

The metal distribution experiments were set up so that the concentration of the alkyl phosphoric acid was expressed as grams of reagent per milliliter of solvent. Since the other concentrations were expressed in moles per liter, it was necessary to convert the reagent concentrations to the same units.

The basis of the conversion was the experimentally determined densities of known solutions containing amyl alcohol and the monoalkyl phosphate. These indicated a specific volume of the reagents in solution according to Table VI.

TABLE VI

SPECIFIC VOLUMES OF THE ALKYL PHOSPHATES IN AMYL ALCOHOL SATURATED WITH WATER

Compound	Specific volume 24°C.
BuH_2PO_4	0.800 ml/gm
AmH_2PO_4	0.846
$HexH_2PO_4$	0.864
$OctH_2PO_4$	0.915

With this table, grams of reagent added to a milliliter of solvent were converted to milliliters of reagent added to a milliliter of solvent. Both the total volume and the number of moles used were then known, and the molarity was determined in the usual fashion. The conversion is sufficiently accurate because even large errors in the reagent volume introduce only small errors in the total volume.

The Distribution of Acids Between Immiscible Solvents

The partition of an acid between water and an organic solvent is represented by the over-all Equation 14.

$$mHQ_{(o)} \rightleftarrows nHQ_{(w)} + n'H^+_{(w)} + n'Q^-_{(w)} \qquad \text{Eq. 14}$$

The concentration of each species is governed by the independent Equations 15 and 16. Equation 15 represents the reversible extraction of un-ionized acid. The concentration

of the un-ionized acid in the water phase is C, and the concentration of the un-ionized acid in the organic phase is DC according to the definition of the distribution coefficient.

$$\begin{array}{cccc} HQ_{(o)} & \rightleftarrows & HQ_{(w)} & \text{Eq. 15} \\ DC & & C & \text{concentrations} \end{array}$$

where $D = \frac{[HQ]_{(o)}}{[HQ]_{(w)}}$

Equation 16 represents the ionization of the acid in the aqueous phase. If the total concentration of acid in the water phase is $\frac{C}{1-\alpha}$ and a fraction, α, of this acid ionizes, then $\frac{C}{1-\alpha}(1-\alpha)$ or C moles per liter of un-ionized acid remain, and $C\frac{\alpha}{1-\alpha}$ moles per liter of both hydrogen ion and acid anion are produced. This is indicated by Equation 16.

$$\begin{array}{cccccc} HQ_{(w)} & \rightleftarrows & Q^-_{(w)} & + & H^+_{(w)} & \text{Eq. 16} \\ C & & \frac{\alpha}{1-\alpha}C & & \frac{\alpha}{1-\alpha}C & \text{concentrations} \end{array}$$

where C = concentration of HQ in water (un-ionized).

The total concentration of the acid in each phase is given in Equation 17.

DC	$\frac{1}{1-\alpha}C$	Eq. 17
Total acid concentration in organic phase	Total acid concentration in water	

In this work the logarithm of the total concentration in each phase was plotted. The slope of this plot has a fundamental significance and is obtained by differentiating the logarithm of the total concentration in each phase and then dividing the differential expression for the water phase by the differential expression for the organic phase. The actual manipulations are indicated below.

Organic phase	Water phase
$\text{Log } DC$	$\text{Log } \frac{1}{1-\alpha}C$
$\text{Log } D + \text{Log } C$	$-\text{Log}(1-\alpha) + \text{Log } C$
$0 + \frac{dC}{C}$	$\frac{d}{1-\alpha} + \frac{dC}{C}$

$$\text{slope} = 1 + \frac{C}{1-\alpha}\cdot\frac{d}{dC} \qquad \text{Eq. 18}$$

In order to express Equation 18 more simply the equilibrium constant of Equation 16 is differentiated and solved for $\frac{d\alpha}{dC}$.

$$k = \left[\frac{\alpha}{1-\alpha}\right]^2 C \qquad \text{Eq. 16 equilibrium constant}$$

$$\frac{d}{dC} = \frac{-\alpha.(1-\alpha)}{2C} \qquad \text{differentiation and simplification} \qquad \text{Eq. 19}$$

Equation 20 is obtained when Equation 18 and Equation 19 are combined.

$$\text{slope} = 1 - \frac{\alpha}{2} \qquad \text{Eq. 20}$$

This particular derivation can be supplied only to those cases where the extraction corresponds to the reaction given by Equation 14. Many extractions follow more complicated paths, for polymerization can occur in either phase. These polymerized forms in turn can be completely or partially ionized. An extensive analysis of the various possibilities is, of course, very desirable but is beyond the scope of this work. It should be recognized that the coefficients of the over-all reaction involving the metal ion are dependent upon the degree of polymerization of the phosphoric acids. However, this information was not available, and as implied in the next section, it was assumed that no polymerization took place for those species occurring in the over-all reaction.

The Coefficients of the Over-all Reaction

The activity coefficients were not known and concentrations are used instead of activities in this work. The concentration of the metal ions was small, and the amount of reagent consumed in complex formation was negligible. No correction was applied for the metal ion concentration or the reagent consumed.

The change of the metal distribution coefficient with a change in reagent concentration indicates the number of

molecules of reagent involved in the over-all reaction. (See pages 21 to 25). The following procedure for measuring the coefficients was used.

The metal distribution coefficient, D_M, and the monoalkyl phosphoric acid concentration were plotted as the absicissa and ordinate respectively at constant acid concentration on log-log graph paper. To obtain this slope, $\frac{\Delta \text{ Log } D_M}{\Delta \text{ Log } [RH_2PO_4]_{(o)}}$, corresponding linear lengths along each axis on the log-log plot were measured. The slope is defined by both the delta expression used above and the differential expression, $\frac{\partial \text{ Log } D_M}{\partial \text{ Log } [RH_2PO_4]_{(o)}}$, since Log $[RH_2PO_4]_{(o)}$ versus Log D_M is a straight line, and the slope is a constant. It was assumed that all of the alkyl phosphoric acid dissolved in the organic phase. The actual distribution of the reagent probably is not important when it is predominately dissolved in the organic phase because of the opposing effects of Equations 4, 5, and 6 versus Equation 7.

The change in the metal distribution coefficient, D_M, with change of acid concentration was calculated. For the purpose of this particular calculation only two acid concentrations were available. Therefore, the alkyl phosphoric acid concentration was arbitrarily chosen from the graph so

that the geometric mean of the two distribution coefficients was one. In a number of unreported experiments the slope, $\frac{\partial \text{Log } D_M}{\partial \text{Log}\left[H^+\right]_{(w)}}$, remained constant from 0.125 M to 1.25 M nitric acid concentrations. Therefore, $\frac{\Delta \text{Log } D_M}{\Delta \text{Log}\left[H^+\right]_{(w)}}$, is safely used for changes in concentration from 0.125 M to 0.312 M nitric acid.

V. RESULTS

The Distribution of Monoalkyl Phosphoric Acids

The partition of the alkyl phosphoric acids between water and ether is given in Table VII and in Figure I. The low value for the slope on the log-log plot of the octyl derivative is due to appreciable ionization of the monooctyl phosphoric acid in the water phase. Most of the octyl derivative is dissolved in the ether leaving a very dilute aqueous solution. The more dilute solutions of acids are more highly ionized.

The butyl phosphoric acid is not strong enough[1] to be ionized sufficiently at the concentrations used to account

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[1] As an approximation the monoalkyl orthophosphoric acids are slightly stronger than orthophosphoric acid.

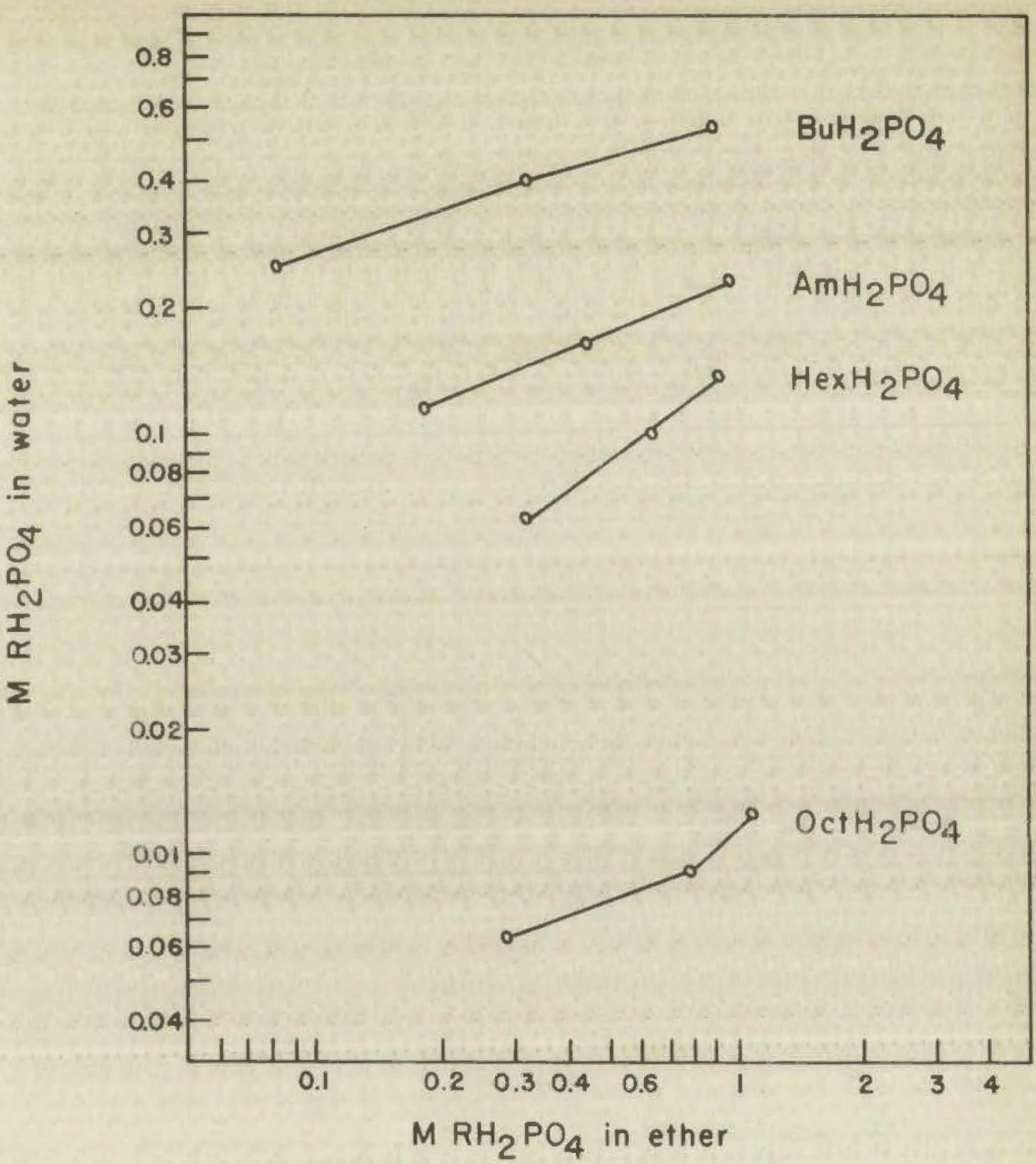

Fig. I. The distribution of RH_2PO_4 between water and ether.

for the low value of the slope on a log-log plot when Equation 20 is considered. However, the slope does indicate considerable dissociation in the water phase. It follows that the acid must associate in the ether phase. The slope at equivalent aqueous concentrations of the log-log plot of each derivative becomes steeper as the length of the carbon chain increases for the three derivatives appreciably soluble in water. This indicates the amount of association in the ether phase decreases as the length of the carbon chain increases.

TABLE VII

THE PARTITION OF RH_2PO_4 BETWEEN WATER AND ETHER AT 26°C.

Compound	Water	Ether
BuH_2PO_4	0.255 M	0.083 M
	0.40	0.32
	0.53	0.89
AMH_2PO_4	0.119 M	0.182 M
	0.164	0.44
	0.232	0.88
$HexH_2PO_4$	0.062 M	0.32 M
	0.099	0.63
	0.139	0.90
	0.202	1.43
$OctH_2PO_4$	0.0063 M	0.288 M
	0.0092	0.78
	0.0121	1.10

The distribution of monoalkyl orthophosphoric acid between water and amyl alcohol is given in Table VIII and in Figure II. The curves flatten when the concentration of the alkyl phosphoric acid in the water phase was less than 0.02 molar due to ionization of the dilute aqueous solutions as Equation 20 predicts. The hexyl and octyl derivatives formed emulsions with amyl alcohol in the water phase. The emulsions formed by the octyl derivative were particularly stable. The water phase was so viscous due to the emulsion of amyl alcohol and octyl phosphoric acid that it would not flow in the centrifuge tube even after centrifuging for two hours. It is believed that the association of the alkyl phosphate and amyl alcohol in the water phase by the hexyl and octyl derivatives causes the curves of the log-log plot to be steeper than predicted by Equation 20.

The monooctyl orthophosphoric acid also forms viscous emulsions in the presence of water and hexane. However, the octyl phosphoric acid when dry dissolves freely in hexane to form a true solution. The presence of water also affects the solubility of the other derivatives in water immiscible solvents. Monobutyl orthophosphoric acid is insoluble in chloroform in the presence of water but is very soluble when water is absent. Solubility of the alkyl phosphates in chloroform and amyl alcohol is explained by the formation of a hydrogen bond between the phosphoryl oxygen and the solvent (22).

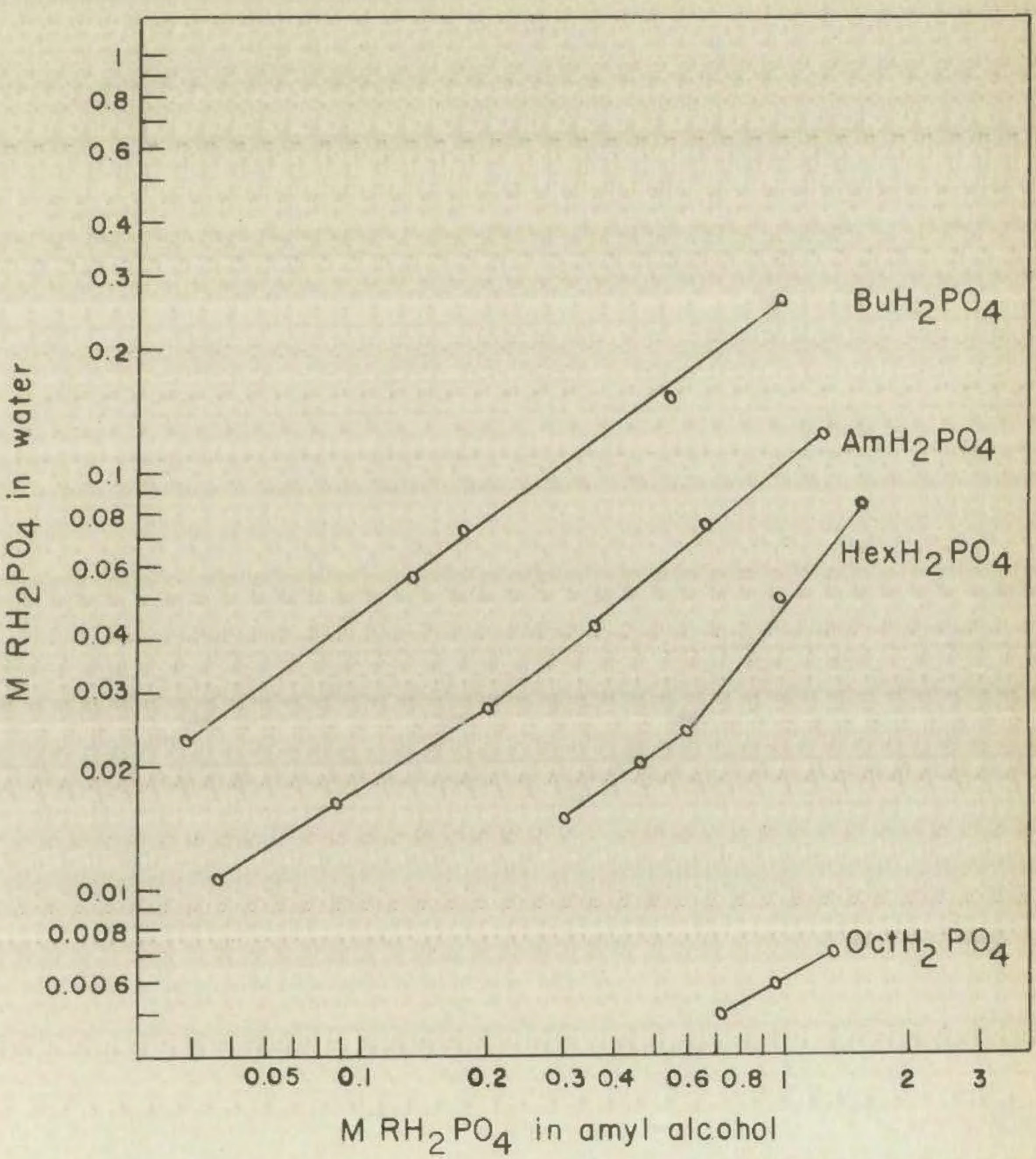

Fig. 2 The distribution of RH$_2$PO$_4$ between water and amyl alcohol.

TABLE VIII

THE DISTRIBUTION OF PHOSPHORIC ACIDS BETWEEN AMYL ALCOHOL AND WATER AT 26°C.

Compound	Water	Amyl alcohol
H_3PO_4	0.38 M	0.0183 M
	0.67	0.035
PrH_2PO_4	0.262 M	0.196 M
	0.35	0.31
	2.21	6.63
BuH_2PO_4	0.023 M	0.039 M
	0.056	0.135
	0.073	0.179
	0.152	0.543
	0.253	1.00
AmH_2PO_4	0.0108 M	0.0460 M
	0.0163	0.090
	0.0276	0.203
	0.043	0.36
	0.075	0.66
	0.125	1.30
$HexH_2PO_4$	0.0149 M	0.31 M
	0.0200	0.47
	0.0242	0.61
	0.049	0.98
	0.084	1.57
$OctH_2PO_4$	0.0049	0.70
	0.0072	1.31

The distribution of the alkyl phosphoric acids in the presence of nitric acid in the amyl alcohol-water system is given in Table IX. No mechanism is suggested for the distribution. However, it is obviously different from the distribution in the absence of nitric acid. Emulsions of the alkyl phosphoric acid and amyl alcohol in water were not formed when nitric acid was present. These samples were centrifuged after they were shaken only to remove drops adhering to the upper portions of the tube.

TABLE IX

THE DISTRIBUTION OF HNO_3 AND RH_2PO_4 BETWEEN WATER AND AMYL ALCOHOL AT 26°C.

Compound	Concentration of RH_2PO_4 in		Concentration of HNO_3 in	
	Water	Amyl alcohol	Water	Amyl alcohol
BuH_2PO_4	0.0738 M	0.267 M	0.146 M	-* M
	0.0660	0.269	0.293	0.0476
	0.0657	0.270	0.550	0.120
	0.0657	0.274	1.025	0.318
	0.140	0.520	0.142	-*
	0.132	0.520	0.289	0.0467
	0.122	0.527	0.563	0.130
	0.119	0.526	1.04	0.330
AmH_2PO_4	0.0429 M	0.217 M	0.145 M	-* M
	0.0421	0.217	0.289	0.0335
	0.0419	0.244	0.554	0.113
	0.0390	0.243	1.046	0.311
	0.0856	0.470	0.139	-*
	0.0850	0.471	0.285	0.0361
	0.0810	0.471	0.561	0.115
	0.0820	0.465	1.06	0.319
$HexH_2PO_4$	0.0411 M	0.319 M	0.1473 M	-* M
	0.0413	0.316	0.294	0.0316
	0.0372	0.312	0.572	0.1127
	0.0386	0.306	1.065	0.310
	0.0720	0.590	0.158	-*
	0.0842	0.585	0.296	0.0390
	0.0822	0.585	0.580	0.1175
	0.0827	0.575	1.098	0.320
$OctH_2PO_4$	-*	0.843 M	0.301 M	0.0466 M
	-*	0.844	0.562	0.106

*These concentrations were too small to determine accurately.

The distribution of each of the metal ions, scandium, yttrium, and lanthanum in a system containing water, amyl alcohol, nitric acid, and one of the monoalkyl phosphoric acids was determined. The results obtained when the alkyl phosphoric acid was contaminated with the corresponding pyrophosphoric acid is given in Table X and Figures III through XIV. The probable composition of the alkyl phosphoric acid was given in Table V. Table XI and Figures XV through XXVI indicate the distributions when the pure monoalkyl orthophosphoric acid was used. The distribution of the metal ions is discussed in the conclusion.

TABLE X

THE DISTRIBUTION COEFFICIENTS* FOR SCANDIUM, YTTRIUM, AND LANTHANUM IN A SYSTEM CONTAINING AMYL ALCOHOL, A MIXTURE OF ALKYL PHOSPHORIC ACIDS†, NITRIC ACID††, AND WATER

Scandium 0.115 M $HNO_{3(Aq)}$		Yttrium 0.115 M $HNO_{3(Aq)}$		Lanthanum 0.115 M $HNO_{3(Aq)}$	
D_{Sc}	BuH_2PO_4 (o)†††	D_Y	BuH_2PO_4 (o)	D_{La}	BuH_2PO_4 (o)
1.23	0.47 M	0.50	0.169M	1.58	0.49 M
4.0	1.41 M	1.07	0.32 M	0.64	0.32 M
4.7	1.64 M	0.280	0.110M	1.80	0.58 M
2.76	0.94 M			1.22	0.48 M

Scandium 0.274 M $HNO_{3(Aq)}$		Yttrium 0.274 M $HNO_{3(Aq)}$		Lanthanum 0.274 M $HNO_{3(Aq)}$	
D_{Sc}	BuH_2PO_4 (o)	D_Y	BuH_2PO_4 (o)	D_{La}	BuH_2PO_4 (o)
0.83	0.95 M	0.249	0.139 M	0.62	0.49 M
3.3	3.1 M	0.83	0.34 M	1.82	0.85 M
1.62	1.72 M	0.67	0.31 M	1.03	0.60 M
2.60	2.56 M			1.18	0.66 M

TABLE X (continued)

Scandium
0.274 M $HNO_{3(Aq)}$

D_{Sc}	$AmH_2PO_{4\,(o)}$
6.2	3.2 M
1.89	1.10 M
7.1	3.56 M
1.94	1.34 M

Yttrium
0.115 M $HNO_{3(Aq)}$

D_Y	$AmH_2PO_{4\,(o)}$
0.59	0.092 M
1.75	0.205 M
3.3	0.368 M
0.83	0.118 M

Lanthanum
0.115 M $HNO_{3(Aq)}$

D_{La}	$AmH_2PO_{4\,(o)}$
0.65	0.100 M
2.07	0.263 M
1.62	0.215 M
3.1	0.38 M

Scandium
0.521 M $HNO_{3(Aq)}$

D_{Sc}	$AmH_2PO_{4(o)}$
0.194	0.72 M
1.22	2.27 M
0.82	1.93 M
3.9	5.11 M

Yttrium
0.274 M $HNO_{3(Aq)}$

D_Y	$AmH_2PO_{4(o)}$
0.98	0.230 M
0.37	0.120 M
0.48	0.134 M
1.20	0.240 M

Lanthanum
0.274 M $HNO_{3(Aq)}$

D_{La}	$AmH_2PO_{4(o)}$
0.662	0.249 M
0.257	0.132 M
1.92	0.51 M
2.25	0.70 M

Scandium
0.115 M $HNO_{3(Aq)}$

D_{Sc}	$HexH_2PO_{4(o)}$
1.83	0.321 M
16.5	1.28 M
3.5	0.47 M
1.30	0.236 M

Yttrium
0.115 M $HNO_{3(Aq)}$

D_Y	$HexH_2PO_{4(o)}$
0.59	0.046 M
0.78	0.066 M
1.90	0.178 M
2.55	0.188 M

Lanthanum
0.115 M $HNO_{3(Aq)}$

D_{La}	$HexH_2PO_{4(o)}$
0.47	0.044 M
5.2	0.267 M
0.95	0.094 M
2.27	0.165 M

Scandium
0.274 M $HNO_{3(Aq)}$

D_{Sc}	$HexH_2PO_{4(o)}$
0.56	0.59 M
9.6	3.1 M
0.220	0.271 M
2.54	1.20 M

Yttrium
0.274 M $HNO_{3(Aq)}$

D_Y	$HexH_2PO_{4(o)}$
0.312	0.095 M
0.78	0.148 M
1.05	0.217 M
1.57	0.242 M

Lanthanum
0.274 M $HNO_{3(Aq)}$

D_{La}	$HexH_2PO_{4(o)}$
2.24	0.350 M
0.186	0.109 M
0.63	0.208 M
0.195	0.140 M
0.83	0.231 M

TABLE X (continued)

Scandium		Yttrium		Lanthanum	
0.115 M $HNO_{3(Aq)}$		0.115 M $HNO_{3(Aq)}$		0.115 M $HNO_{3(Aq)}$	
D_{Sc}	$OctH_2PO_{4(o)}$	D_Y	$OctH_2PO_{4(o)}$	D_{La}	$OctH_2PO_{4(o)}$
0.40	0.122 M	0.65	0.045 M	0.229	0.054 M
3.2	0.45 M	1.34	0.068 M	1.59	0.162 M
1.27	0.265 M	2.31	0.097 M	0.68	0.109 M
0.70	0.182 M	4.70	0.148 M	0.60	0.099 M
				0.199	0.050 M
				0.63	0.101 M

Scandium		Yttrium		Lanthanum	
0.274 M $HNO_{3(Aq)}$		0.274 M $HNO_{3(Aq)}$		0.274 M $HNO_{3(Aq)}$	
D_{Sc}	$OctH_2PO_{4(o)}$	D_Y	$OctH_2PO_{4(o)}$	D_{La}	$OctH_2PO_{4(o)}$
0.131	0.262 M	0.168	0.079 M	0.047	0.071 M
1.02	0.83 M	0.37	0.115 M	0.0245	0.048 M
2.88	1.57 M	0.44	0.132 M	0.34	0.218 M
0.66	0.69 M	0.83	0.182 M	0.0036	0.0133M
				0.77	0.46 M
				0.22	0.150 M

*The distribution coefficient and the concentrations were rounded off so that the error introduced was no greater than three percent.

†The monoalkyl orthophosphoric acid was contaminated by the corresponding dialkyl pyrophosphoric acid according to Table V.

††The concentration of nitric acid is given for the water phase, and the alkyl phosphoric acid concentration is given for the amyl alcohol phase.

†††The true concentration of the alkyl phosphoric acid in the amyl alcohol for all the scandium distribution is found by multiplying the value given in Table X by 0.001.

TABLE XI

THE DISTRIBUTION COEFFICIENTS FOR SCANDIUM, YTTRIUM, AND LANTHANUM IN A SYSTEM CONTAINING AMYL ALCOHOL, WATER, NITRIC ACID*, AND MONOALKYL ORTHOPHOSPHORIC† ACID

Scandium		Yttrium		Lanthanum	
0.115 M $HNO_{3(Aq)}$		0.143 M $HNO_{3(Aq)}$		0.143 M $HNO_{3(Aq)}$	
D_{Sc}	$BuH_2PO_{4(o)}$[††]	D_Y	$BuH_2PO_{4(o)}$	D_{La}	$BuH_2PO_{4(o)}$
3.7	1.64 M	0.56	0.68 M	0.268	0.45 M
0.37	0.60 M	1.47	0.93 M	0.066	0.59 M
3.6	1.72 M	2.12	1.08 M	0.125	0.76 M
1.81	1.19 M	0.75	0.78 M	0.37	1.02 M
0.75	0.76 M				
1.09	0.99 M				

Scandium		Yttrium		Lanthanum	
0.274 M $HNO_{3(Aq)}$		0.274 M $HNO_{3(Aq)}$		0.274 M $HNO_{3(Aq)}$	
D_{Sc}	$BuH_2PO_{4(o)}$	D_Y	$BuH_2PO_{4(o)}$	D_{La}	$BuH_2PO_{4(o)}$
2.85	3.11 M	0.42	0.94 M	0.284	1.29 M
0.45	1.40 M	0.57	1.01 M	0.0319	0.66 M
1.15	2.23 M	0.125	0.66 M	0.080	0.89 M
0.155	0.96 M	0.66	1.07 M	0.186	1.14 M

TABLE XI (continued)

Scandium 0.115 M $HNO_{3(Aq)}$		Yttrium 0.143 M $HNO_{3(Aq)}$		Lanthanum 0.143 M $HNO_3(Aq)$	
D_{Sc}	$AmH_2PO_{4(o)}$	D_Y	$AmH_2PO_{4(o)}$	D_{La}	$AmH_2PO_{4(o)}$
47	2.58 M	0.103	0.33 M	0.079	0.47 M
20.7	1.80 M	0.66	0.49 M	0.204	0.61 M
0.83	0.60 M	2.05	0.70 M	0.66	0.81 M
73	3.0 M	6.3	0.90 M	1.77	1.03 M

Scandium 0.274 M $HNO_{3(Aq)}$		Yttrium 0.274 M $HNO_{3(Aq)}$		Lanthanum 0.274 M $HNO_{3(Aq)}$	
D_{Sc}	$AmH_2PO_{4(o)}$	D_Y	$AmH_2PO_{4(o)}$	D_{La}	$AmH_2PO_{4(o)}$
0.37	0.92 M	0.134	0.49 M	0.072	0.69 M
7.4	2.52 M	0.43	0.74 M	0.138	0.83 M
1.51	1.44 M	1.18	0.98 M	0.299	1.01 M
3.1	1.96 M	3.2	1.19 M	1.03	1.36 M

Scandium 0.115 M $HNO_{3(Aq)}$		Yttrium 0.143 M $HNO_{3(Aq)}$		Lanthanum 0.143 M $HNO_{3(Aq)}$	
D_{Sc}	$HexH_2PO_{4(o)}$	D_Y	$HexH_2PO_{4(o)}$	D_{La}	$HexH_2PO_{4(o)}$
1.85	0.70 M	0.211	0.35 M	0.222	0.53 M
0.260	0.34 M	2.33	0.60 M	0.403	0.60 M
4.7	0.96 M	0.70	0.47 M	0.80	0.75 M
41	1.95 M	0.048	0.23 M	1.83	0.94 M

Scandium 0.274 M $HNO_{3(Aq)}$		Yttrium 0.274 M $HNO_{3(Aq)}$		Lanthanum 0.274 M $HNO_{3(Aq)}$	
D_{Sc}	$HexH_2PO_{4(o)}$	D_Y	$HexH_2PO_{4(o)}$	D_{La}	$HexH_2PO_4(o)$
0.74	1.07 M	0.192	0.54 M	0.120	0.72 M
7.2	2.43 M	0.74	0.66 M	0.198	0.82 M
10.5	2.74 M	1.21	0.82 M	0.32	0.95 M
38	4.1 M	0.0263	0.31 M	0.73	1.19 M

TABLE XI (continued)

Scandium 0.115 M $HNO_{3(Aq)}$		Yttrium 0.143 M $HNO_{3(Aq)}$		Lanthanum 0.143 M $HNO_{3(Aq)}$	
D_{Sc}	$OctH_2PO_{4(o)}$	D_Y	$OctH_2PO_{4(o)}$	D_{La}	$OctH_2PO_{4(o)}$
3.4	0.84 M	0.160	0.37 M	0.0156	0.28 M
18.3	1.35 M	0.53	0.45 M	0.045	0.41 M
39	1.84 M	1.84	0.55 M	0.222	0.38 M
86	3.0 M	3.3	0.66 M	0.96	0.80 M

Scandium 0.274 M $HNO_{3(Aq)}$		Yttrium 0.274 M $HNO_{3(Aq)}$		Lanthanum 0.274 M $HNO_{3(Aq)}$	
D_{Sc}	$OctH_2PO_{4(o)}$	D_Y	$OctH_2PO_{4(o)}$	D_{La}	$OctH_2PO_{4(o)}$
0.067	0.50 M	0.203	0.53 M	0.0137	0.43 M
0.81	1.10 M	0.058	0.39 M	0.0265	0.53 M
3.6	1.83 M	0.090	0.44 M	0.095	0.71 M
8.7	2.43 M	0.84	0.78 M	0.236	0.88 M

*The nitric acid concentration is given for the water phase and the monoalkyl orthophosphoric acid concentration is given for the amyl alcohol phase.

†The monoalkyl orthophosphoric acid was heated on a steam bath for 12 hours with an excess of water. This hydrolyzed any of the pyro form to the ortho form.

††The true concentration of the monoalkyl orthophosphoric acid for the scandium distributions is obtained by multiplying the tabular value by 0.001.

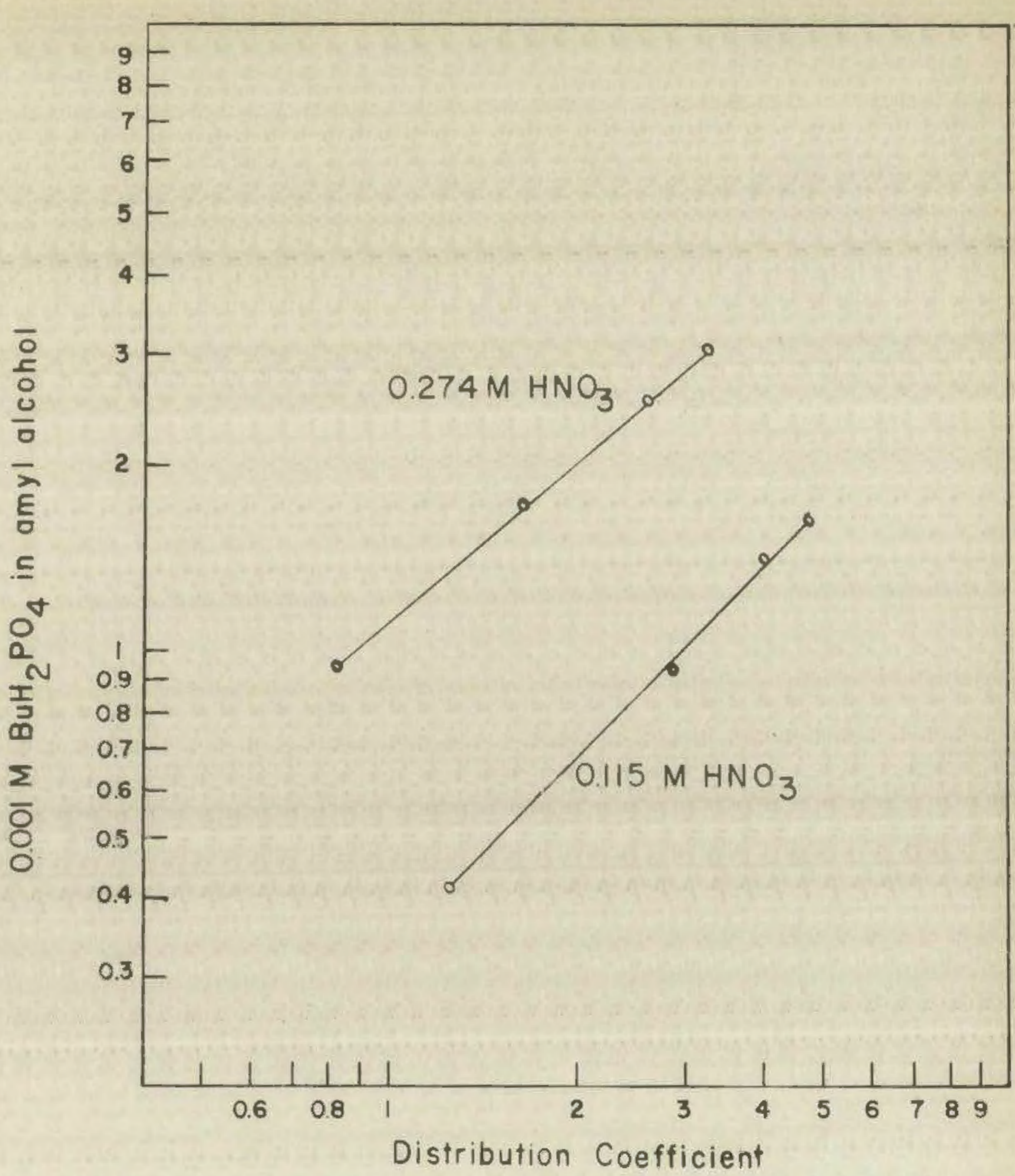

Fig. 3. The hydrogen ion and butyl phosphoric acid dependency of the extraction of scandium into amyl alcohol.

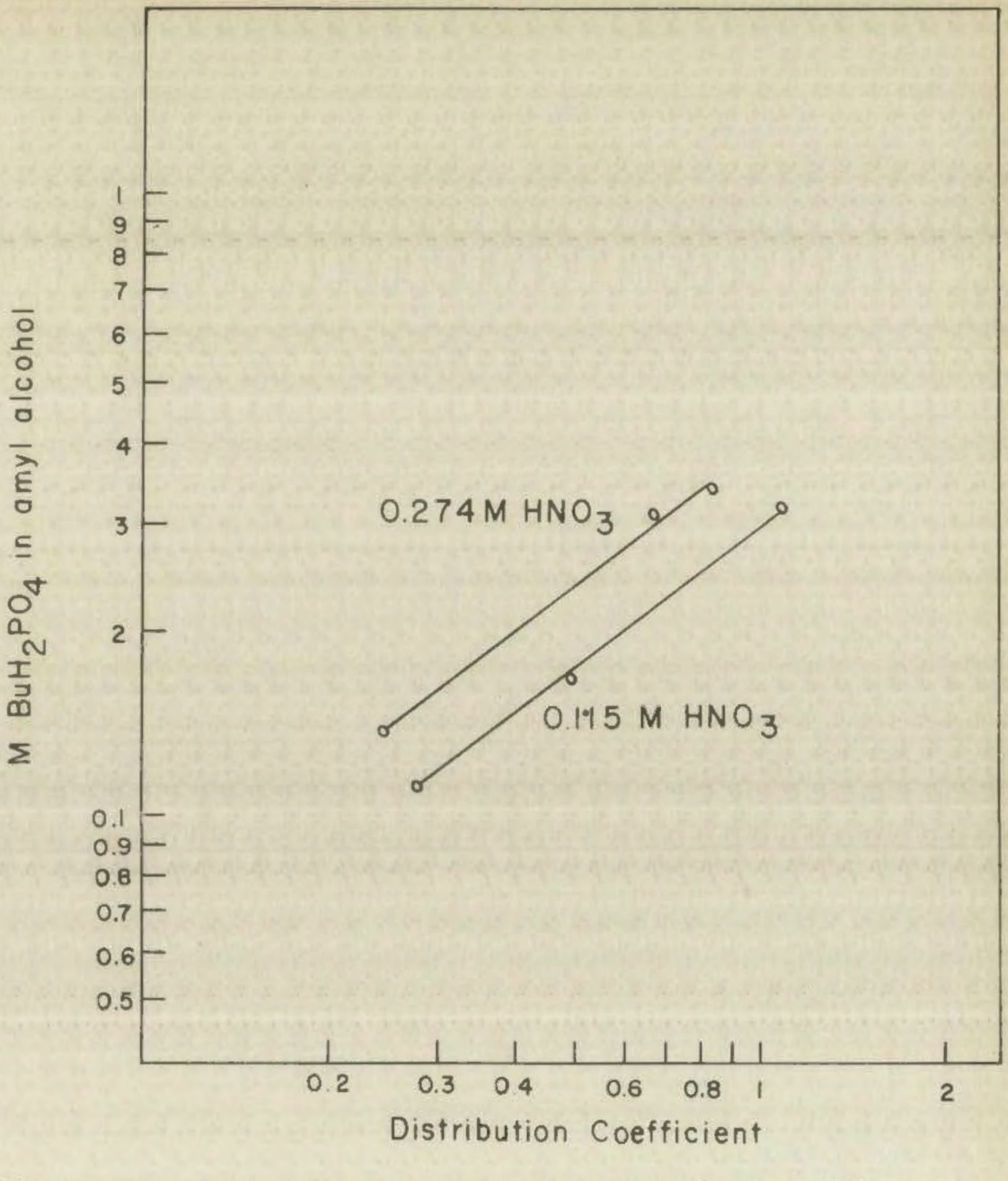

Fig. 4. The hydrogen ion and butyl phosphoric acid dependency of the extraction of yttrium into amyl alcohol.

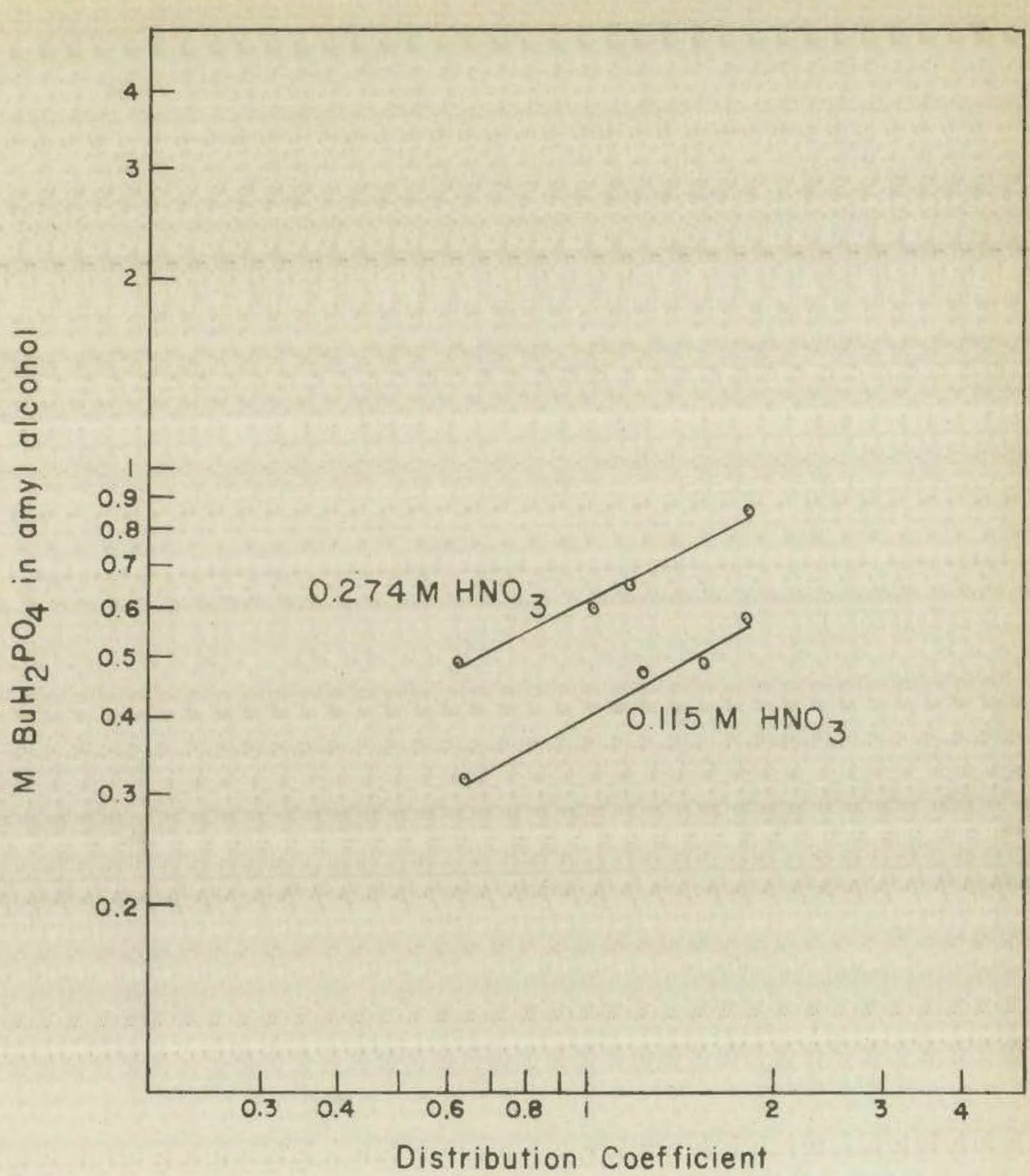

Fig. 5. The hydrogen ion and butyl phosphoric acid dependency of the extraction of lanthanum into amyl alcohol.

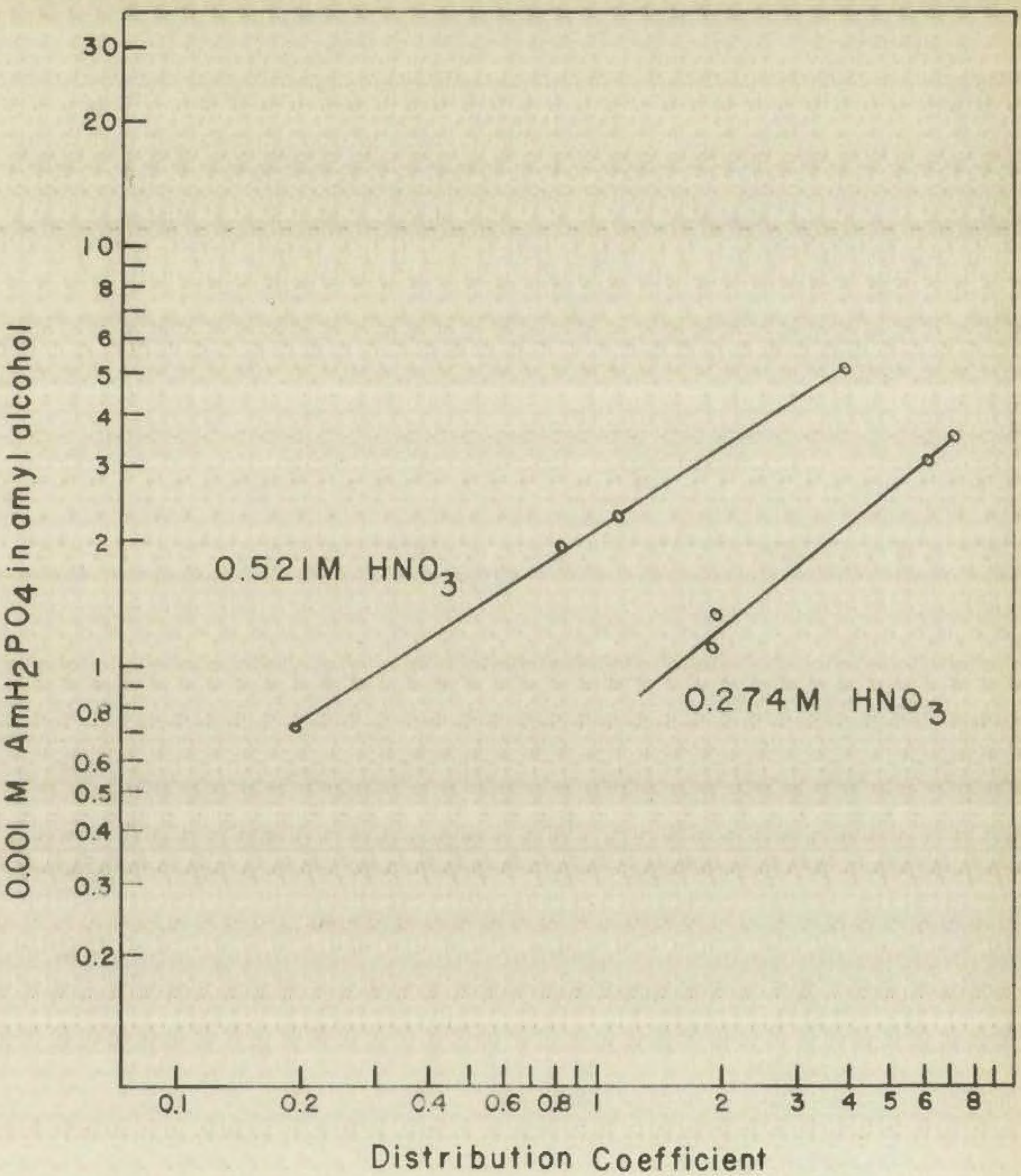

Fig. 6. The hydrogen ion and amyl phosphoric acid dependency of the extraction of scandium into amyl alcohol.

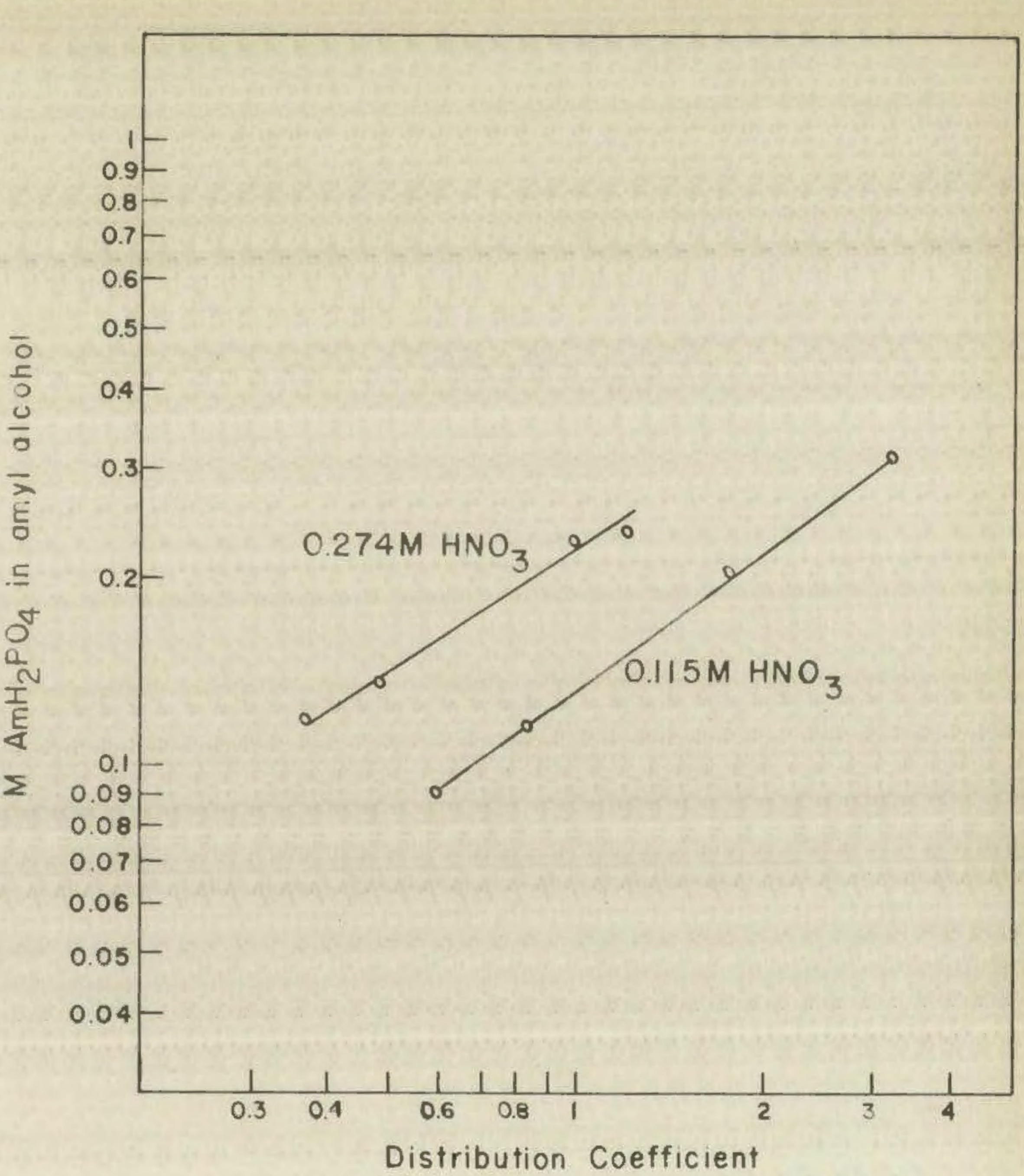

Fig. 7 The hydrogen ion and amyl phosphoric acid dependency of the extraction of yttrium into amyl alcohol.

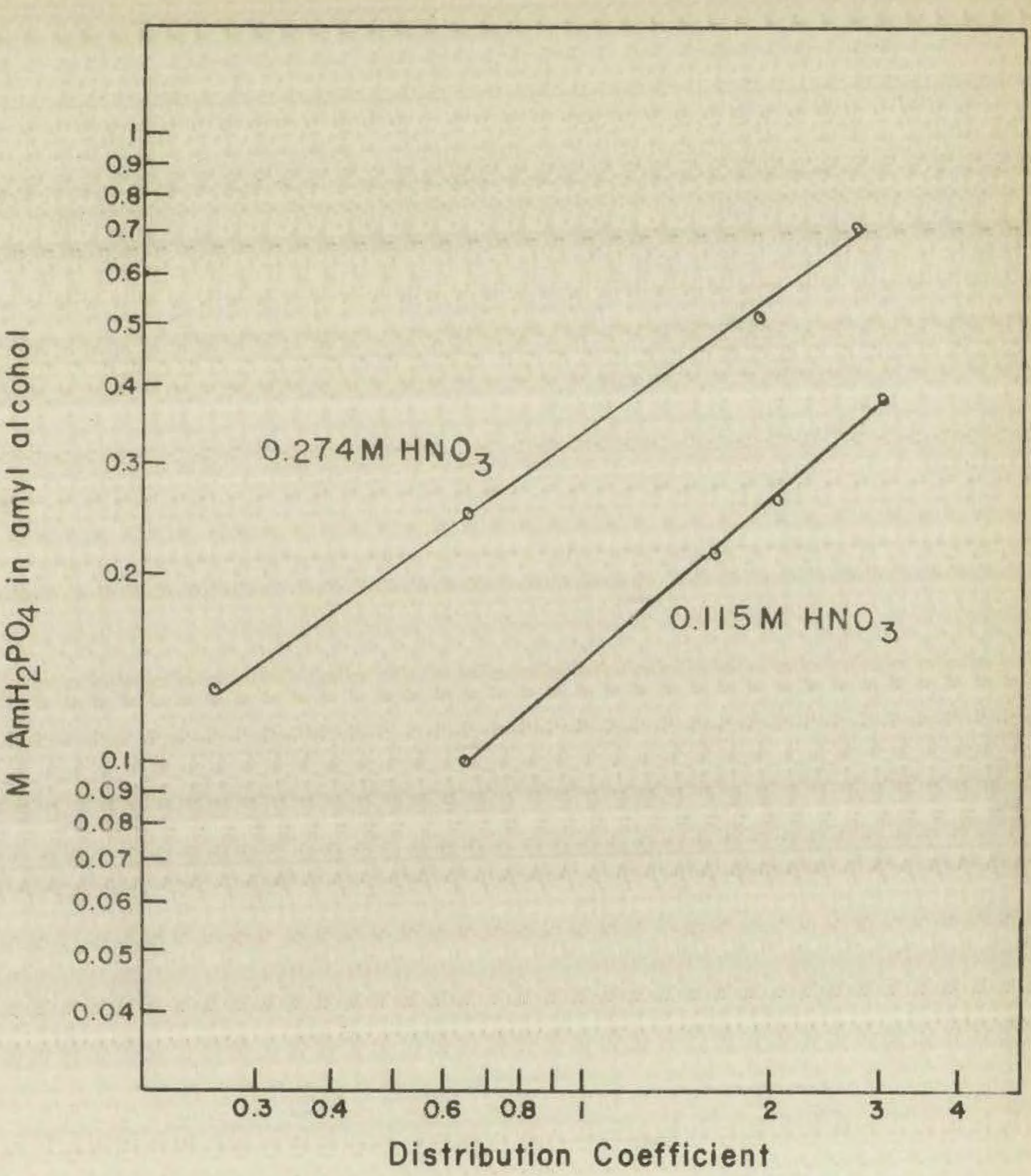

Fig. 8. The hydrogen ion and amyl phosphoric acid dependency of the extraction of lanthanum into amyl alcohol.

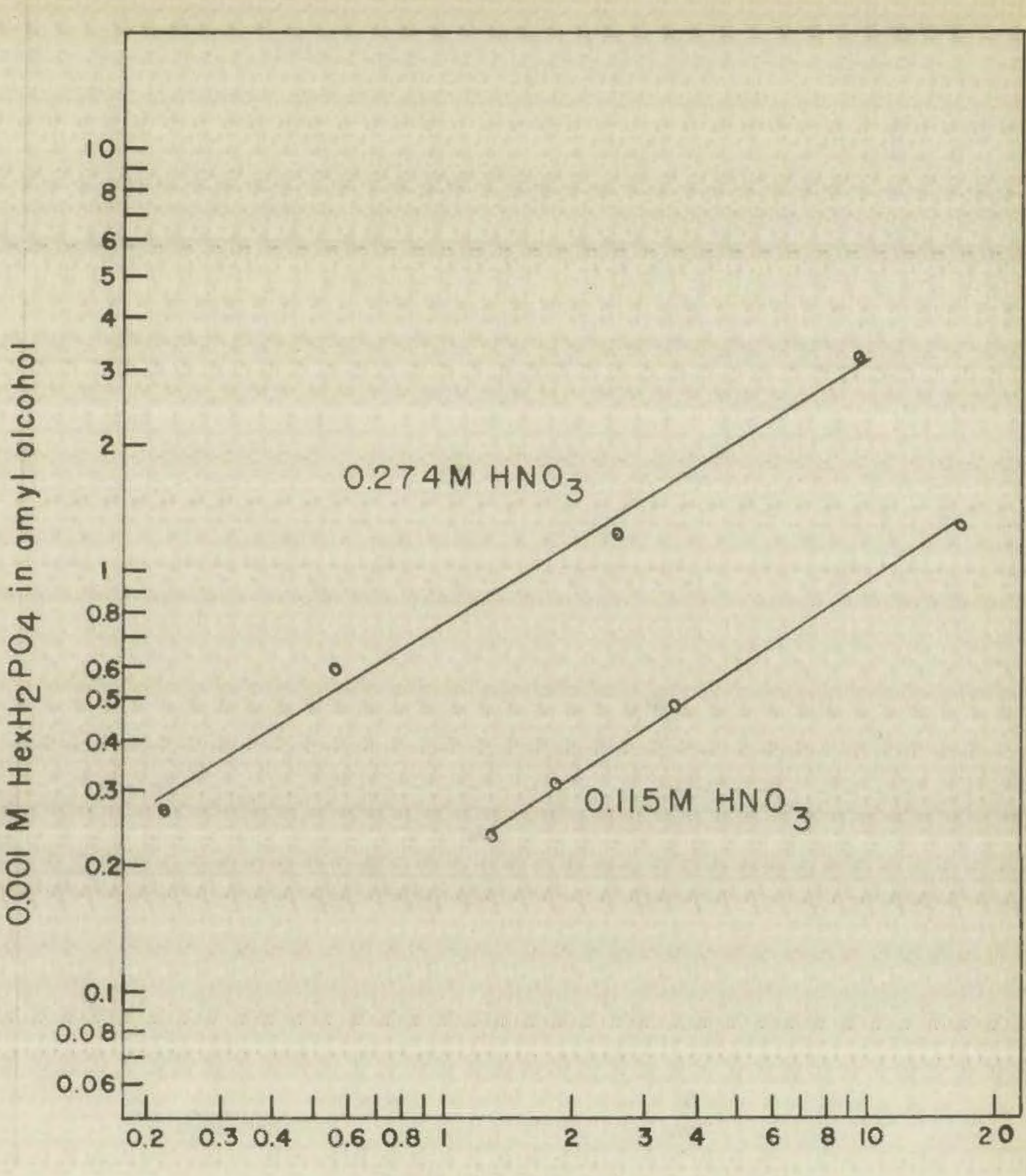

Fig. 9. The hydrogen ion and hexyl phosphoric acid dependency of the extraction of scandium into amyl alcohol.

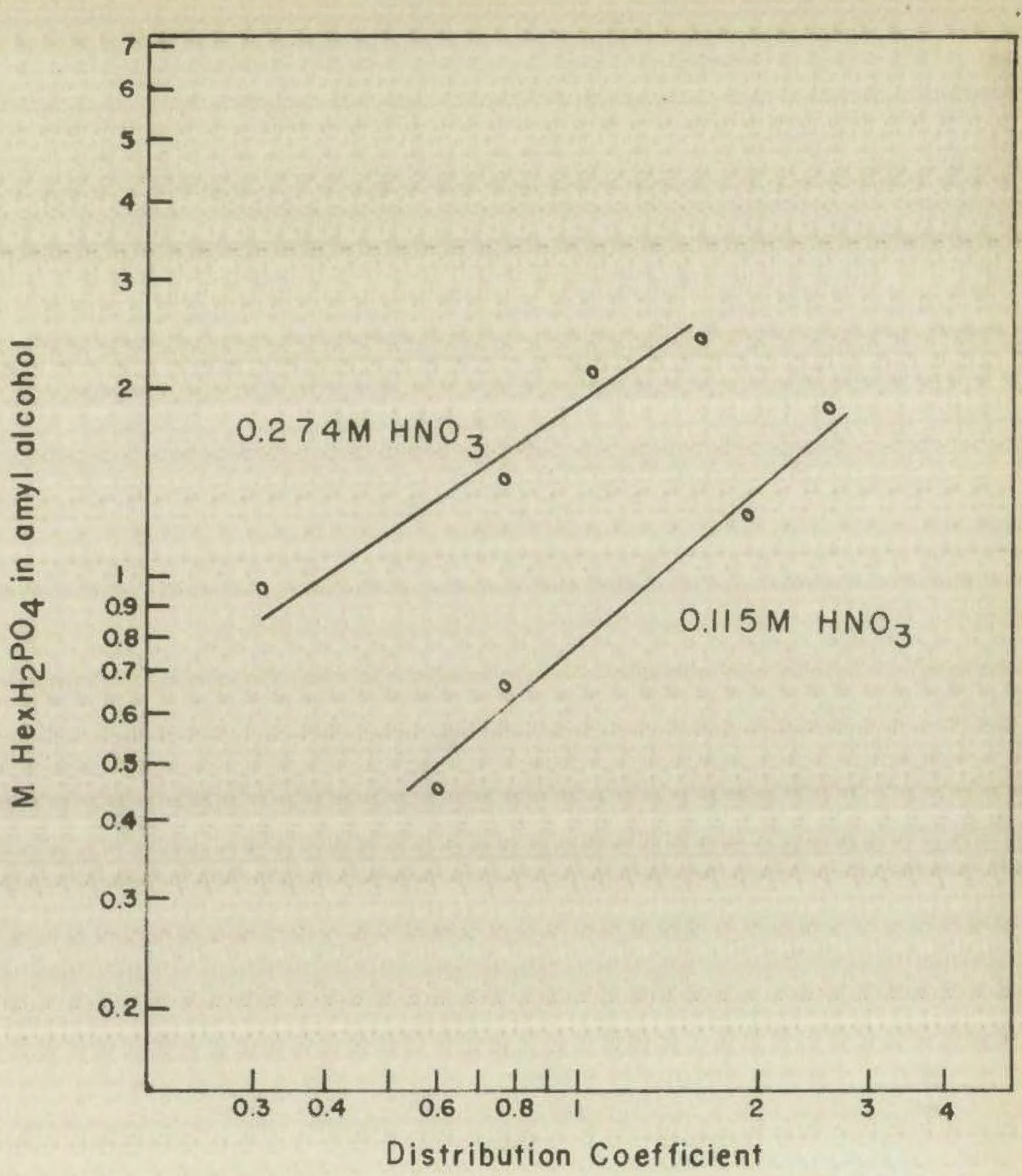

Fig. 10. The hydrogen ion and hexyl phosphoric acid dependency of the extraction of yttrium into amyl alcohol.

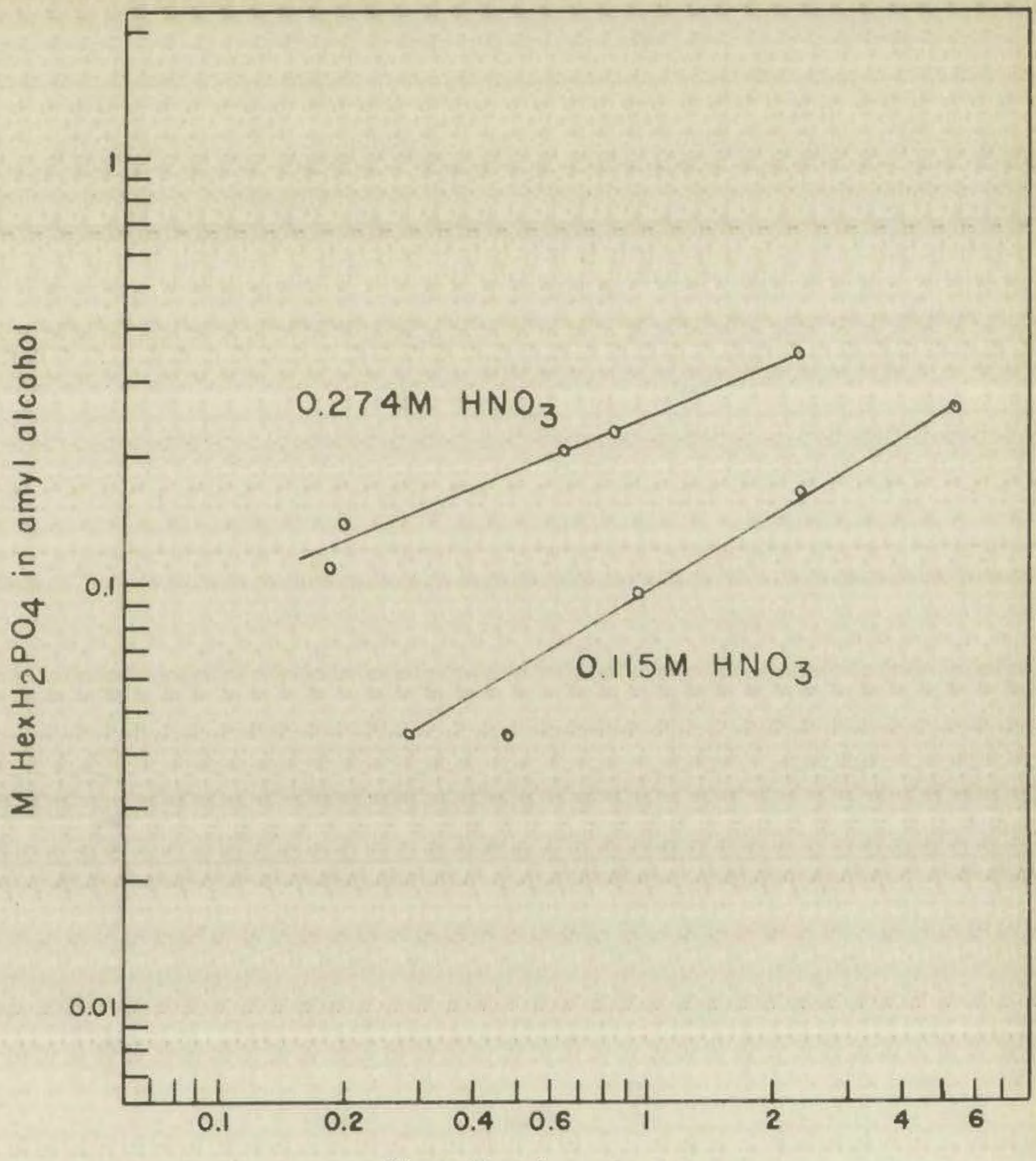

Fig. 11. The hydrogen ion and hexyl phosphoric acid dependency of the extraction of lanthanum into amyl alcohol.

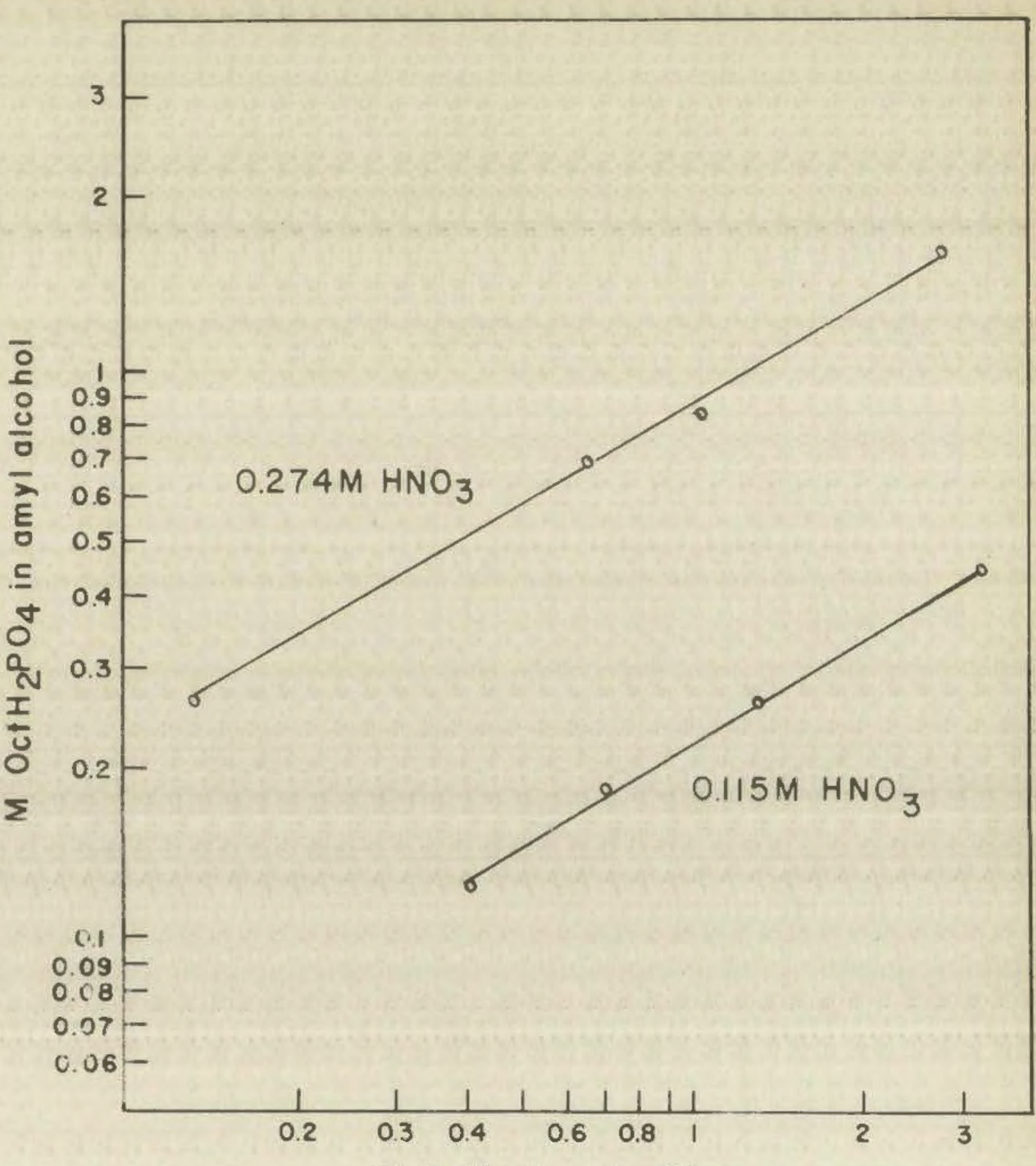

Fig. 12. The hydrogen ion and octyl phosphoric acid dependency of the extraction of scandium into amyl alcohol.

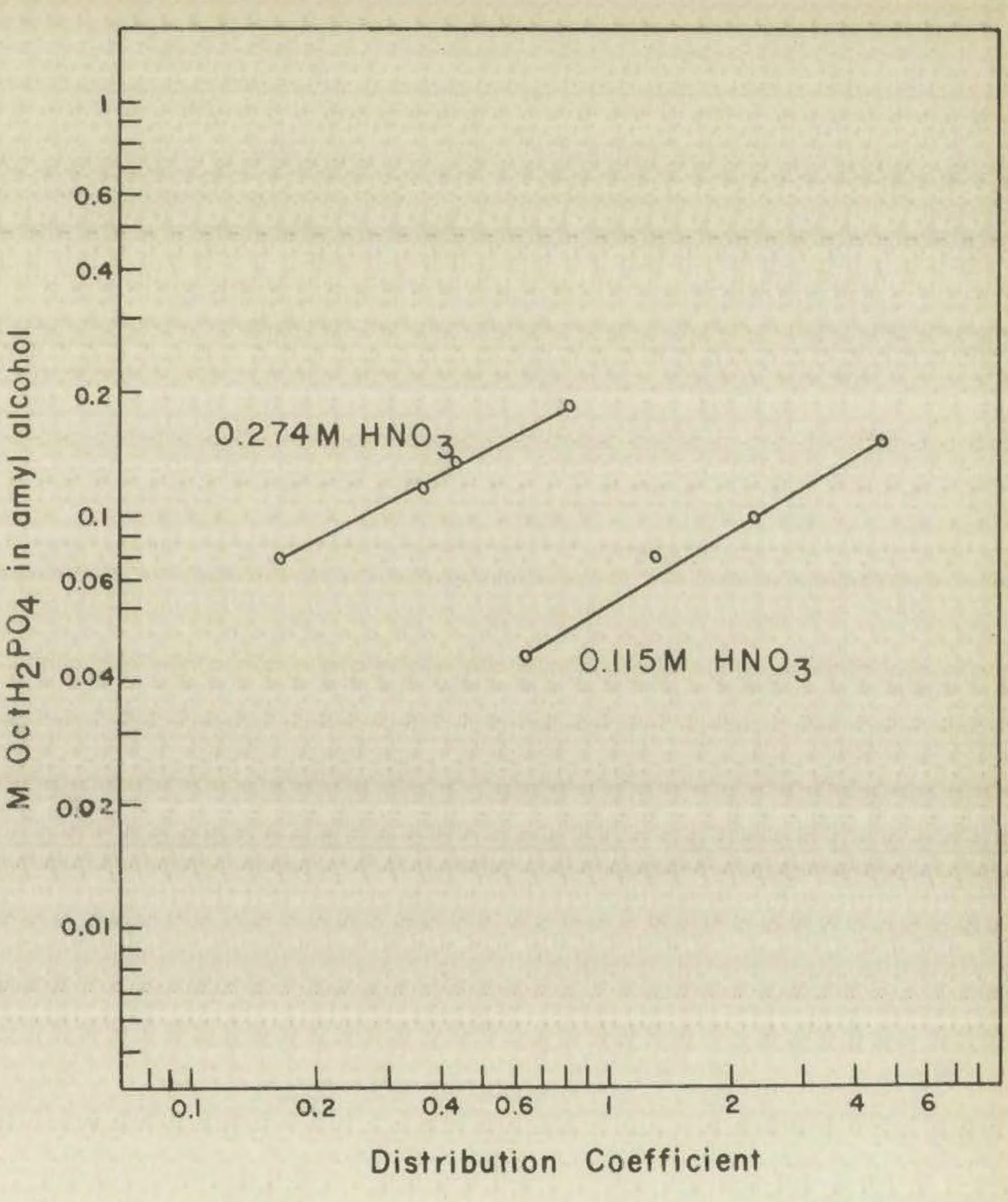

Fig. 13 The hydrogen ion and octyl phosphoric acid dependency of the extraction of yttrium into amyl alcohol.

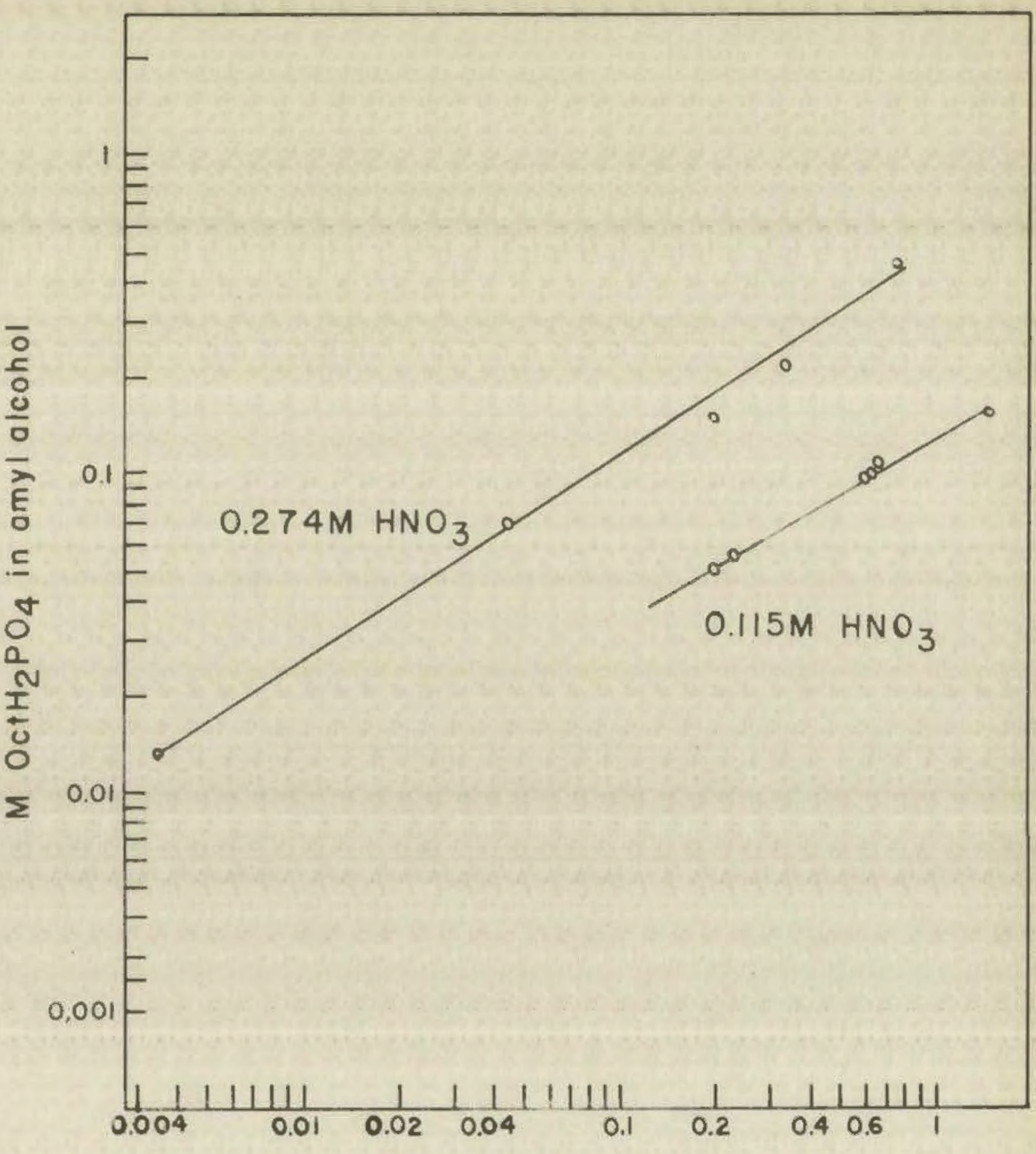

Fig. 14. The hydrogen ion and octyl phosphoric acid dependency of the extraction of lanthanum into amyl alcohol.

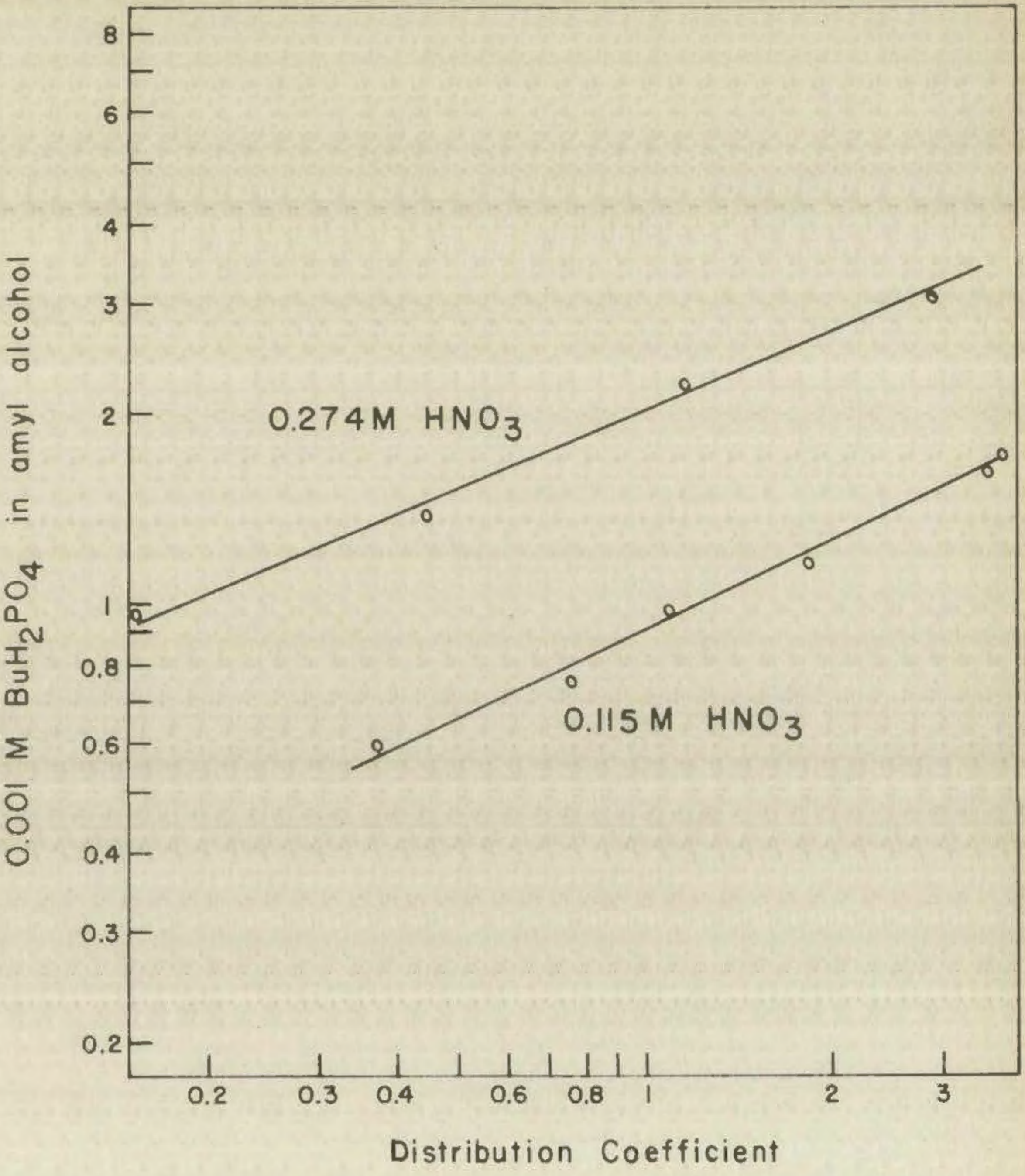

Fig. 15 The hydrogen ion and butyl orthophosphoric acid dependency of the extraction of scandium into amyl alcohol.

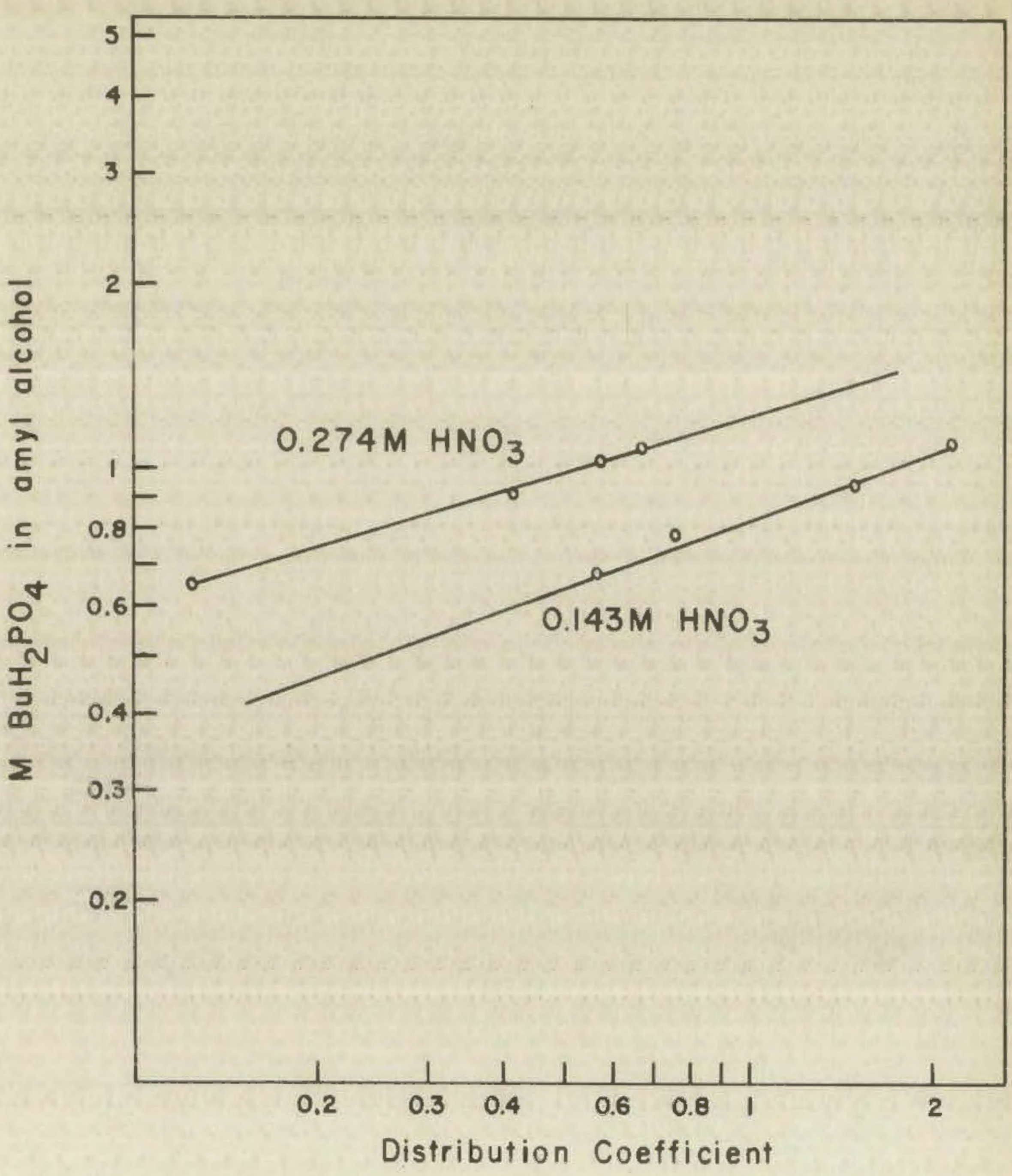

Fig. 16. The hydrogen ion and butyl orthophosphoric acid dependency of the extraction of yttrium into amyl alcohol.

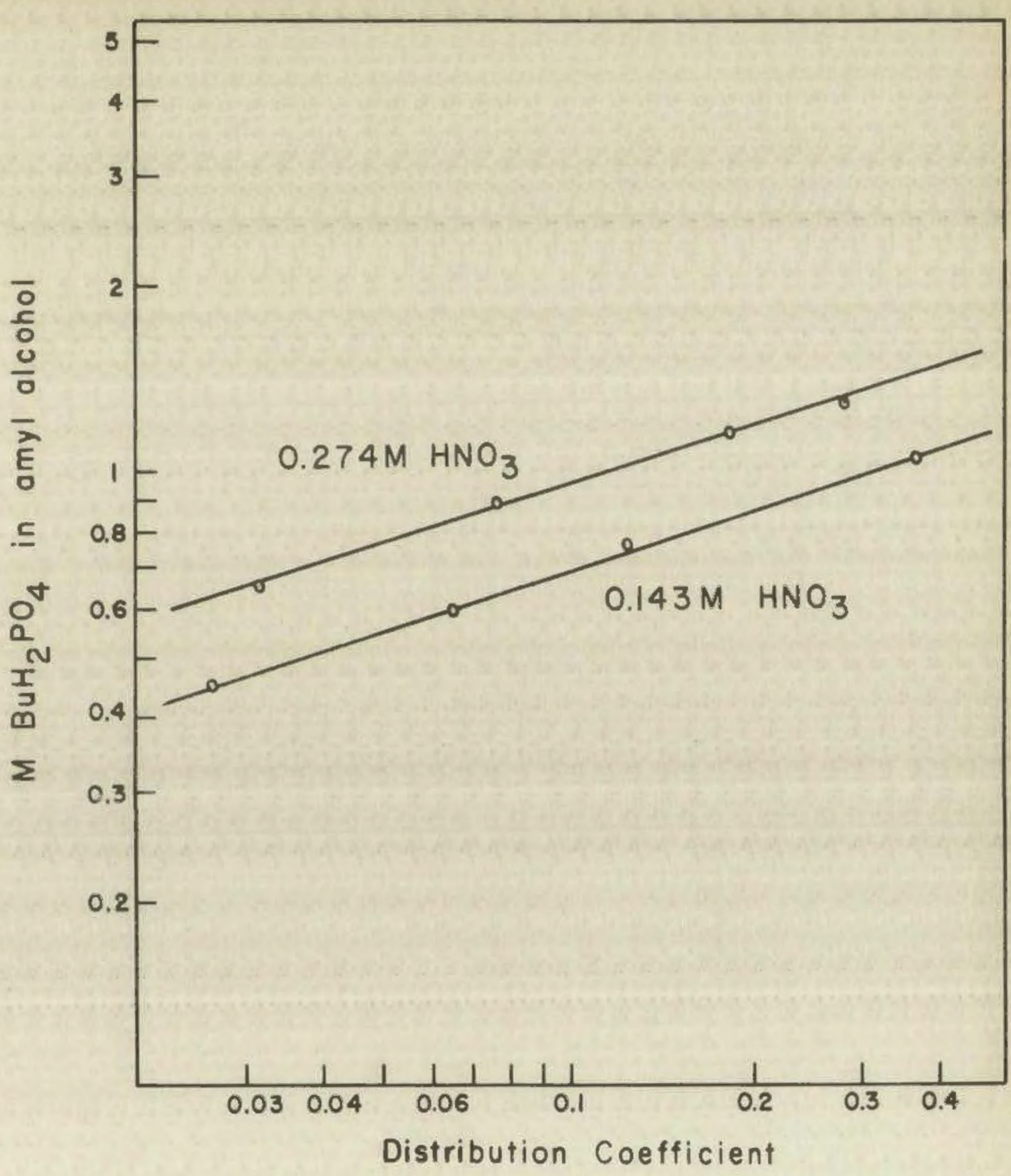

Fig. 17. The hydrogen ion and butyl orthophosphoric acid dependency of the extraction of lanthanum into amyl alcohol.

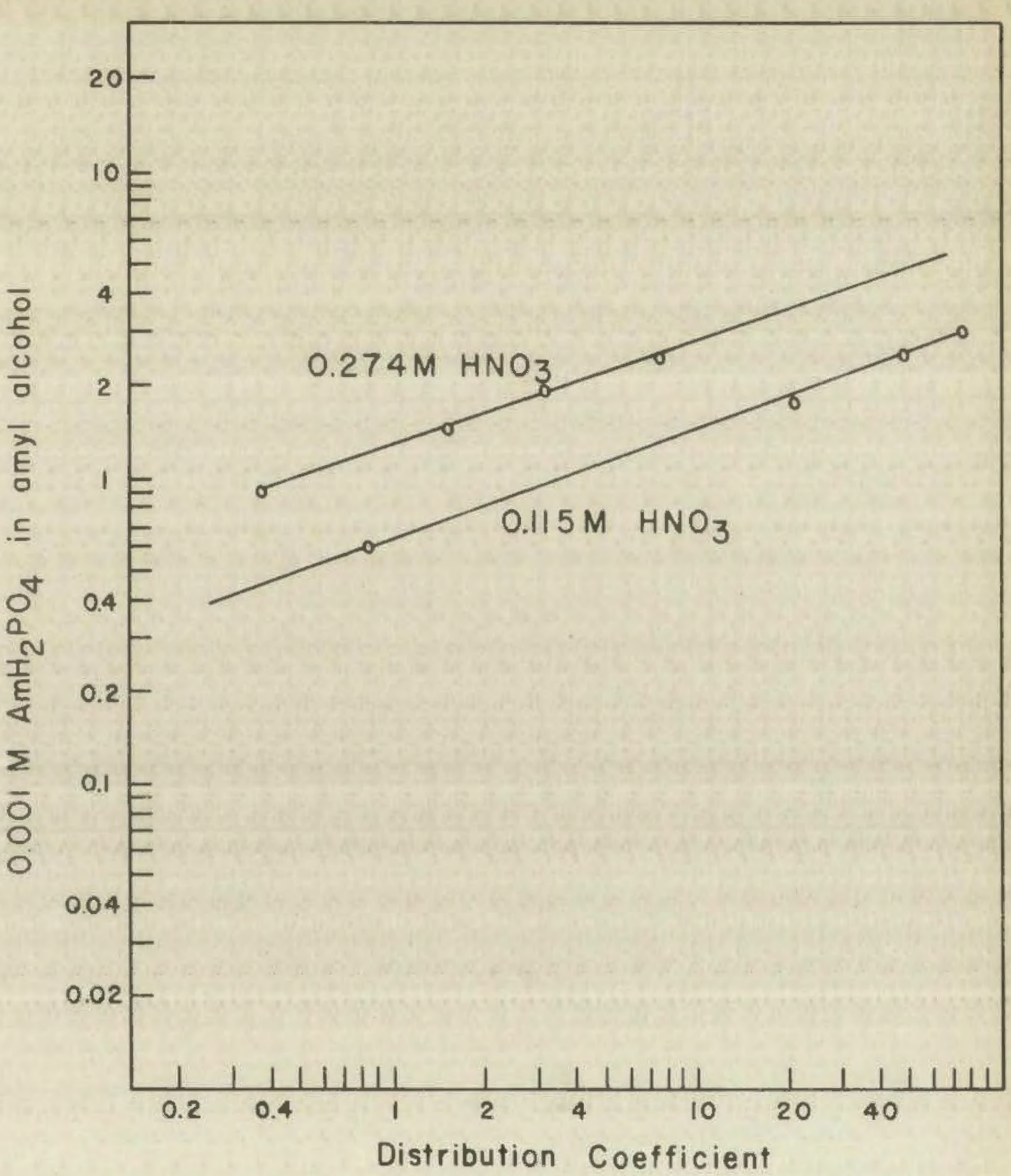

Fig. 18 The hydrogen ion and amyl orthophosphoric acid dependency of the extraction of scandium into amyl alcohol.

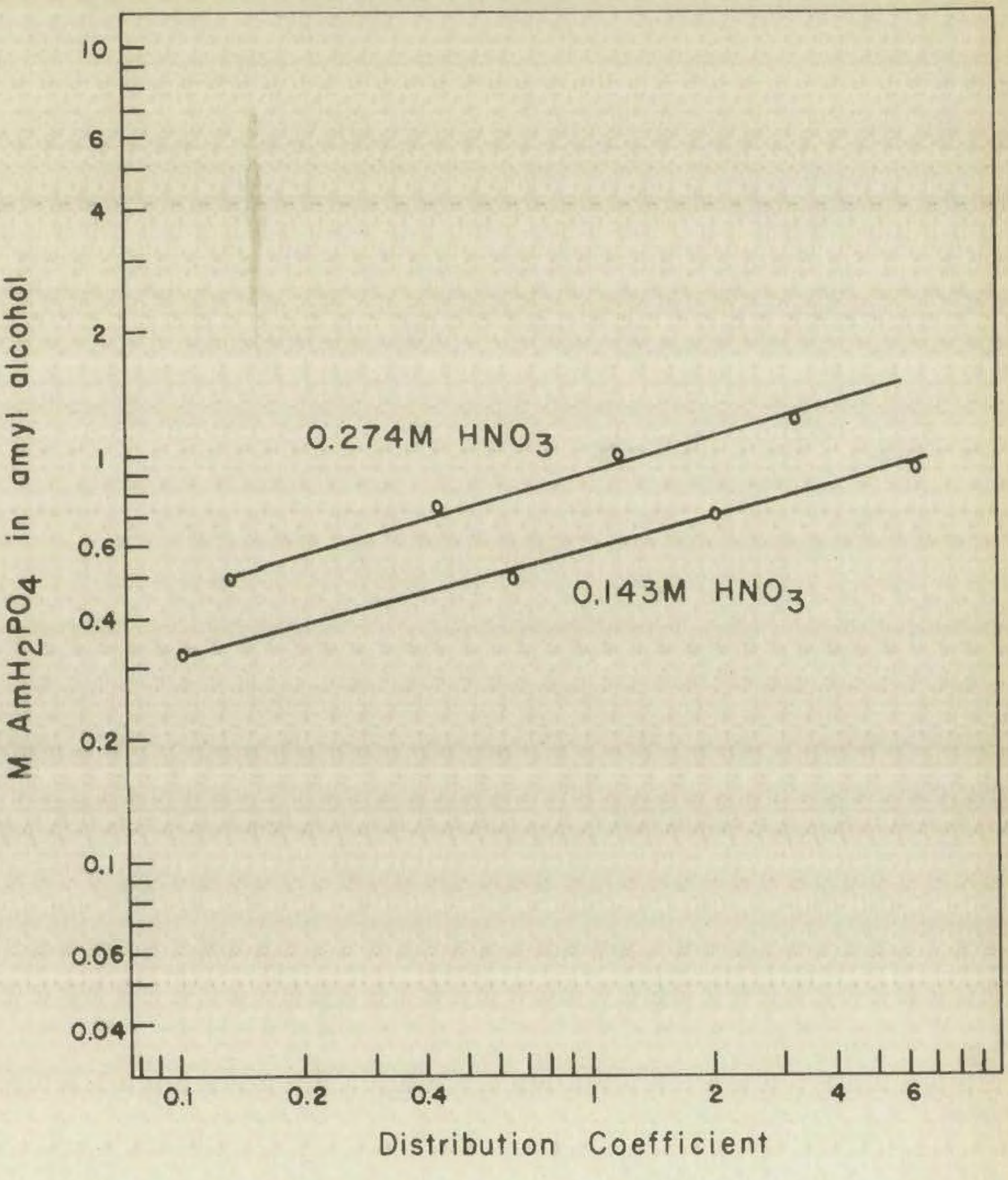

Fig. 19. The hydrogen ion and amyl orthophosphoric acid dependency of the extraction of yttrium into amyl alcohol.

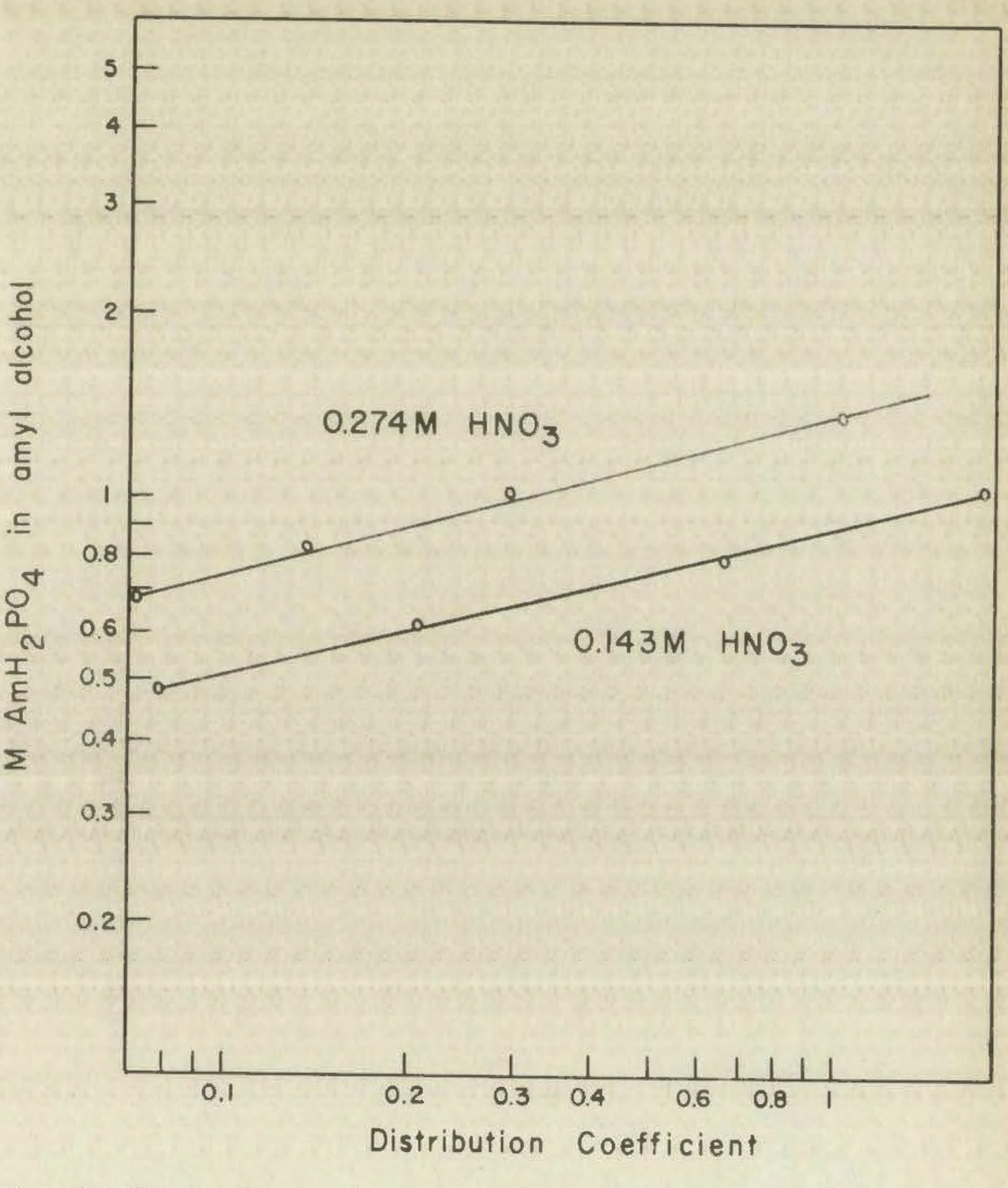

Fig. 20. The hydrogen ion and amyl orthophosphoric acid dependency of the extraction of lanthanum into amyl alcohol.

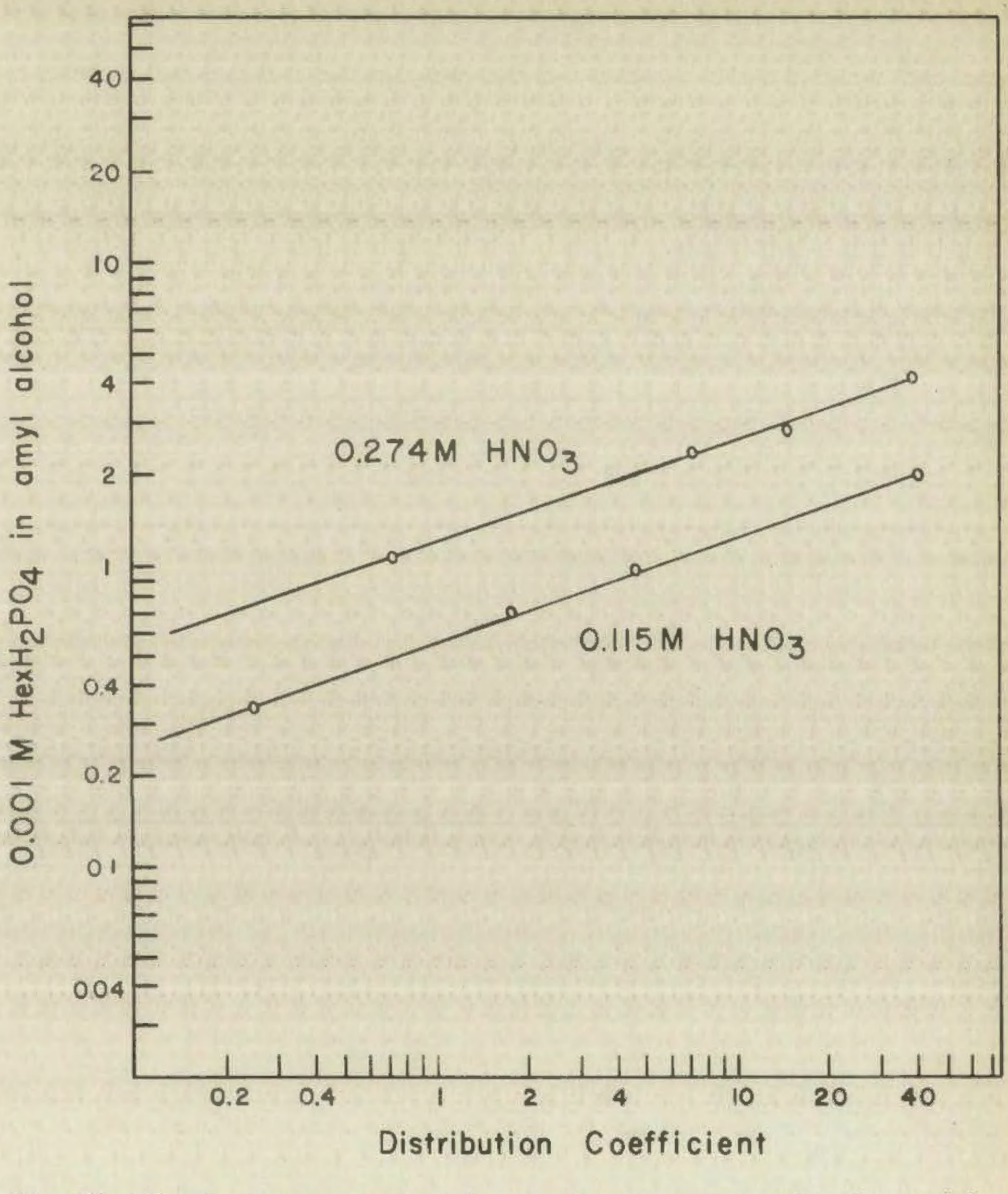

Fig. 21. The hydrogen ion and hexyl orthophosphoric acid dependency of the extraction of scandium into amyl alcohol.

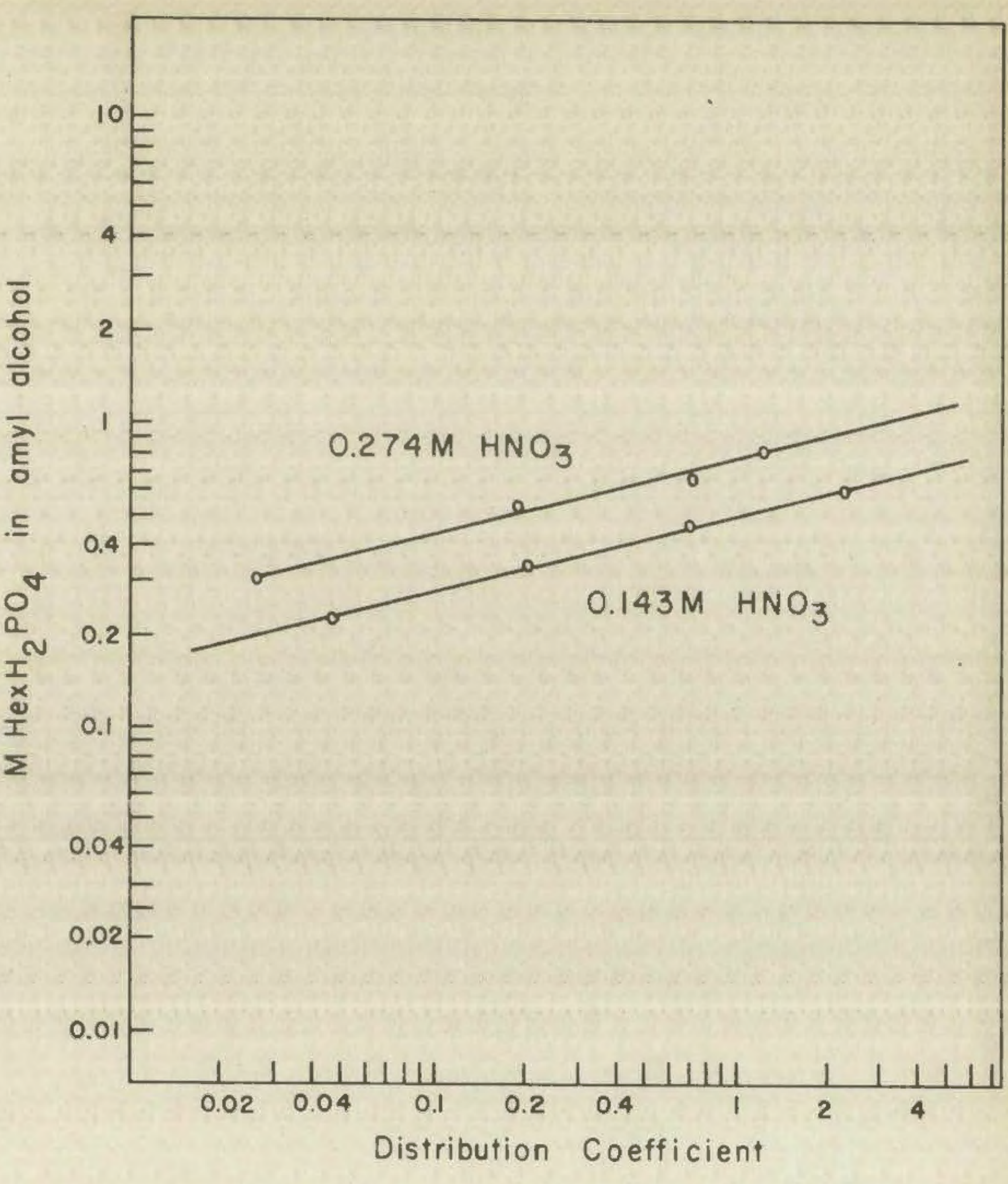

Fig. 22. The hydrogen ion and hexyl orthophosphoric acid dependency of the extraction of yttrium into amyl alcohol.

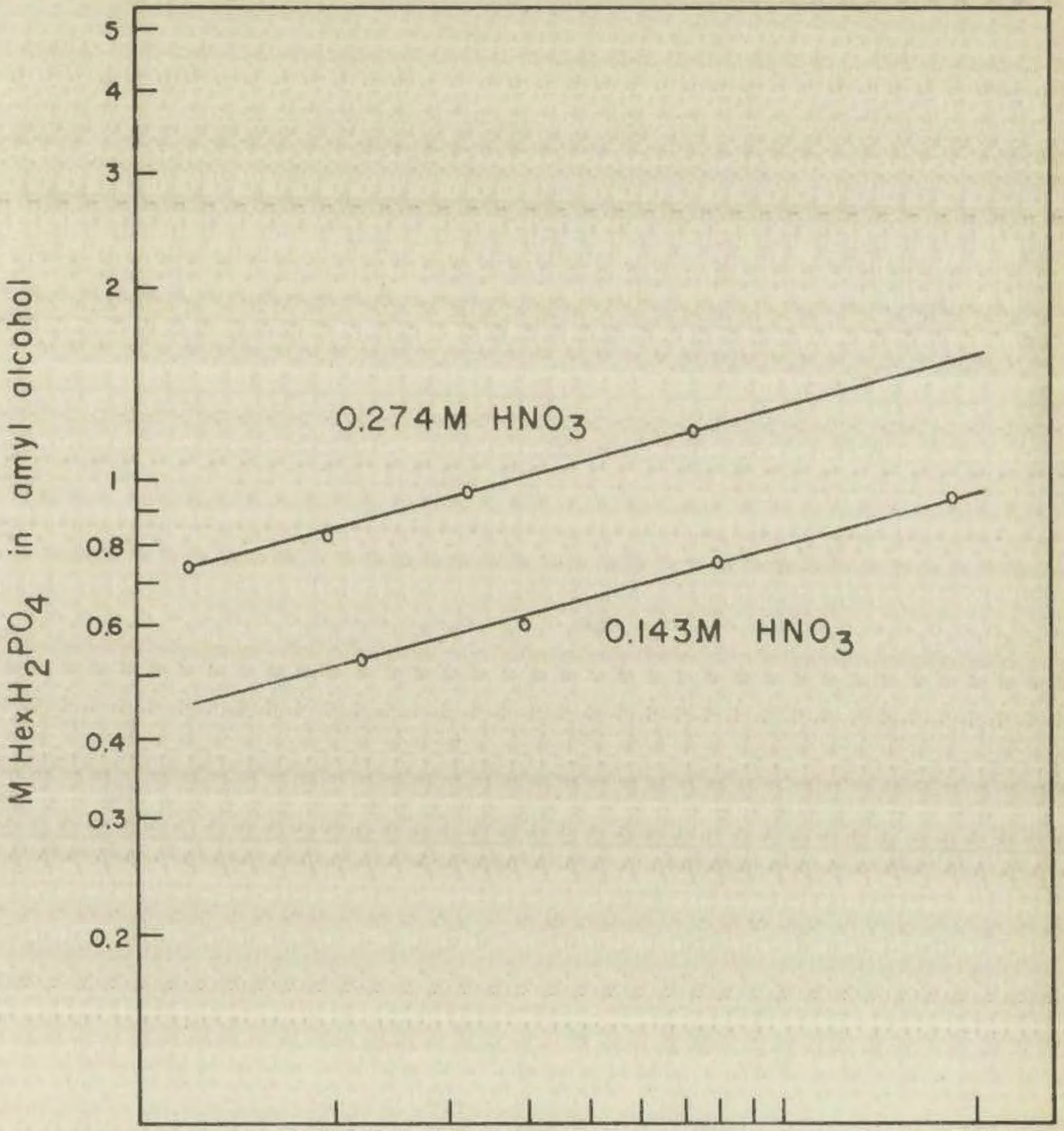

Fig. 23. The hydrogen ion and hexyl orthophosphoric acid dependency of the extraction of lanthanum into amyl alcohol.

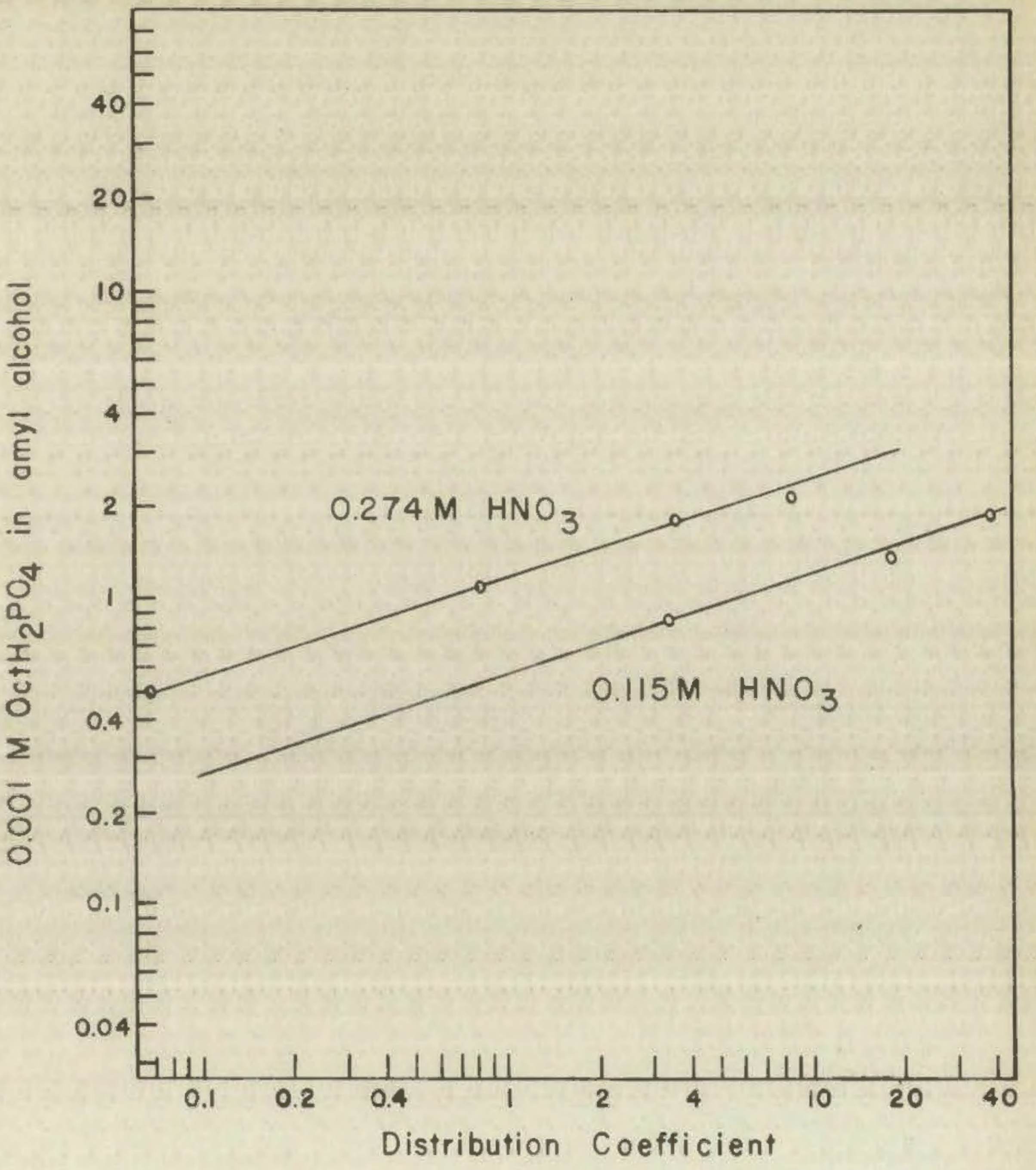

Fig. 24. The hydrogen ion and octyl orthophosphoric acid dependency of the extraction of scandium into amyl alcohol.

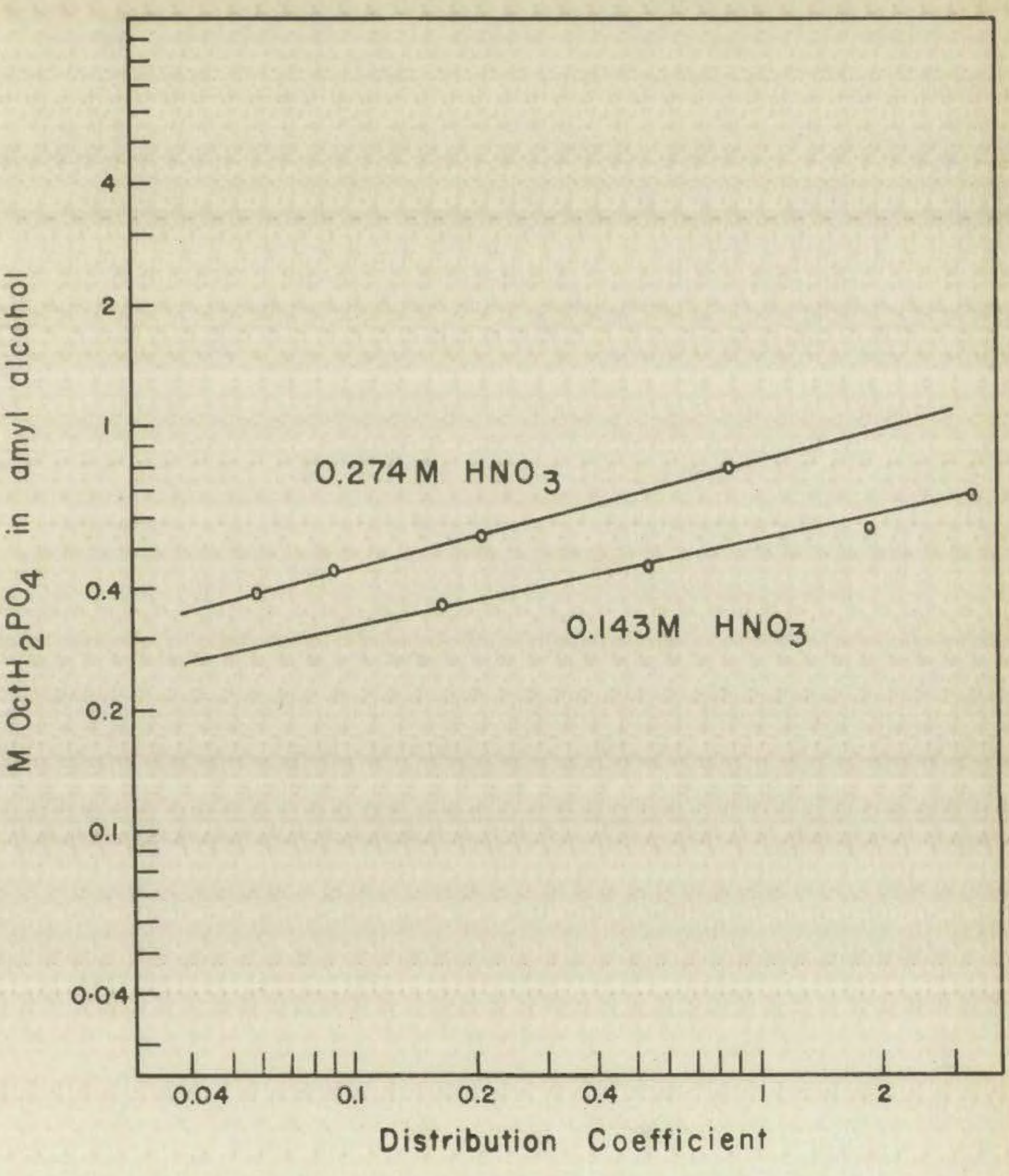

Fig. 25. The hydrogen ion and octyl orthophosphoric acid dependency of the extraction of yttrium into amyl alcohol.

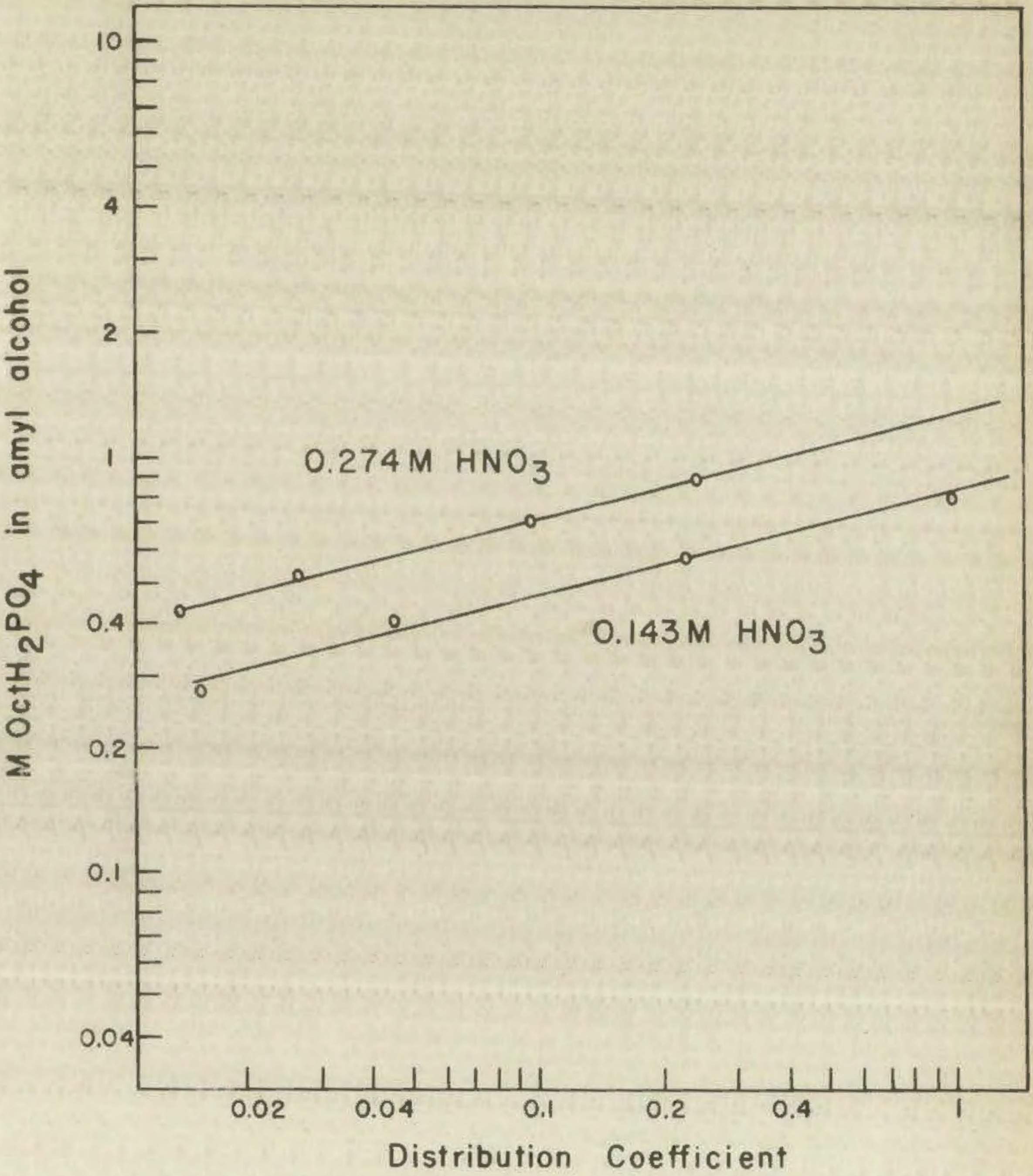

Fig. 26. The hydrogen ion and octyl orthophosphoric acid dependency of the extraction of lanthonum into amyl alcohol.

TABLE XII

PHYSICAL CONSTANTS OF THE MONOALKYL ORTHOPHOSPHORIC ACIDS

Compound	Melting points of the crystalline solids		Estimated* densities of the liquids 24°C.	Calculated† densities of the liquids 24°C.
PrH_2PO_4	35.8°	37.3°C.	----	----
BuH_2PO_4	32.0	33.3	1.250 gm/ml	1.220 gm/ml
AmH_2PO_4	28.0	29.5	1.180	1.177
$HexH_2PO_4$	7.5	8.7	1.154	1.144
$OctH_2PO_4$	27.9	29.4	1.092	1.093

*The estimated densities of the pure liquids were obtained from densities of their amyl alcohol solutions as explained in Calculations.

†The method for calculating the densities is given in Calculations and is based on the reported densities of phosphoric acid and trialkyl phosphates.

VI. CONCLUSIONS

The data for the extraction of the group IIIa ions with the monoalkyl orthophosphoric acids were used to determine the coefficients of the reaction, the equilibrium constants, and the separation factor for the metal ions.

The data for the mixed ortho and pyro acids were not used for these calculations because the results were not based on the use of pure reagents and are difficult to interpret. The pyro acids are much better extracting agents than the ortho acids. For 50 percent extraction of a metal ion and 0.274 nitric acid, it is estimated that the concentration of the pure pyro form required is about 0.03 of concentration of the pure ortho form.

The over-all reaction between monoalkyl orthophosphoric acid and ions of the group IIIa elements is given in Equation 21.

$$M^{+3}_{(w)} + pRH_2PO_{4(o)} \rightleftarrows H_{p-3}M(RHPO_4)_{p(o)} + 3H^{+}_{(w)} \qquad \text{Eq. 21}$$

It is obtained from a balanced equation and the assumption that only neutral species are extracted into the organic phase.

This reaction was studied experimentally by measuring the metal ion distribution coefficient at various acid and reagent concentrations. The coefficients of Equation 21

were calculated from these data as described in Calculations. They are given in Table XIII.

TABLE XIII

THE COEFFICIENTS* OF THE OVER-ALL REACTION

Compound	Scandium p	Scandium h	Yttrium p	Yttrium h	Lanthanum p	Lanthanum h
BuH_2PO_4	2.3	2.0	3.4	1.9	3.2	1.5
AmH_2PO_4	2.8	2.3	3.9	2.8	4.0	2.7
$HexH_2PO_4$	3.0	2.6	4.0	2.9	3.9	2.9
$OctH_2PO_4$	2.8	3.0	3.9	3.0	4.0	2.7

*The coefficients, h and p, are defined by the following equations as well as by Equation 21.

$$p = \frac{\partial \log D}{\partial \log \left[RH_2PO_4\right]_{(o)}} \quad \text{and} \quad h = \frac{\partial \log D}{\partial \log \left[H^+\right]_{(w)}}$$

The coefficients of the reaction of the metal ions and butyl phosphoric acid do not correspond to any simple mechanism. The assumption that the concentration of the complexed metal ions in the water is small compared to the total concentration in the water phase probably is not valid for this derivative, and the over-all reaction of Equation 21 can not be used.

The coefficients obtained for the amyl, hexyl, and octyl phosphoric acids indicate that the following reactions probably occur.

$$Sc^{+3}_{(w)} + 3RH_2PO_{4(o)} \longleftrightarrow Sc(RHPO_4)_{3(o)} + 3H^{+}_{(w)} \qquad \text{Eq. 22}$$

$$Y^{+3}_{(w)} + 4RH_2PO_{4(o)} \longleftrightarrow HY(RHPO_4)_{4(o)} + 3H^{+}_{(w)} \qquad \text{Eq. 23}$$

$$La^{+3}_{(w)} + 4RH_2PO_{4(o)} \longleftrightarrow HLa(RHPO_4)_{4(o)} + 3H^{+}_{(w)} \qquad \text{Eq. 24}$$

These equations correspond to the over-all reaction, Equation 21.

The concentration of the monoalkyl orthophosphoric acid required for 50 percent extraction at 0.274 molar nitric acid is given in Figure XXVII. The effect of the size of the alkyl group reaches a limiting value for the hexyl derivative. Further increases in the length of the carbon chain apparently do not significantly change the ability of the monoalkyl

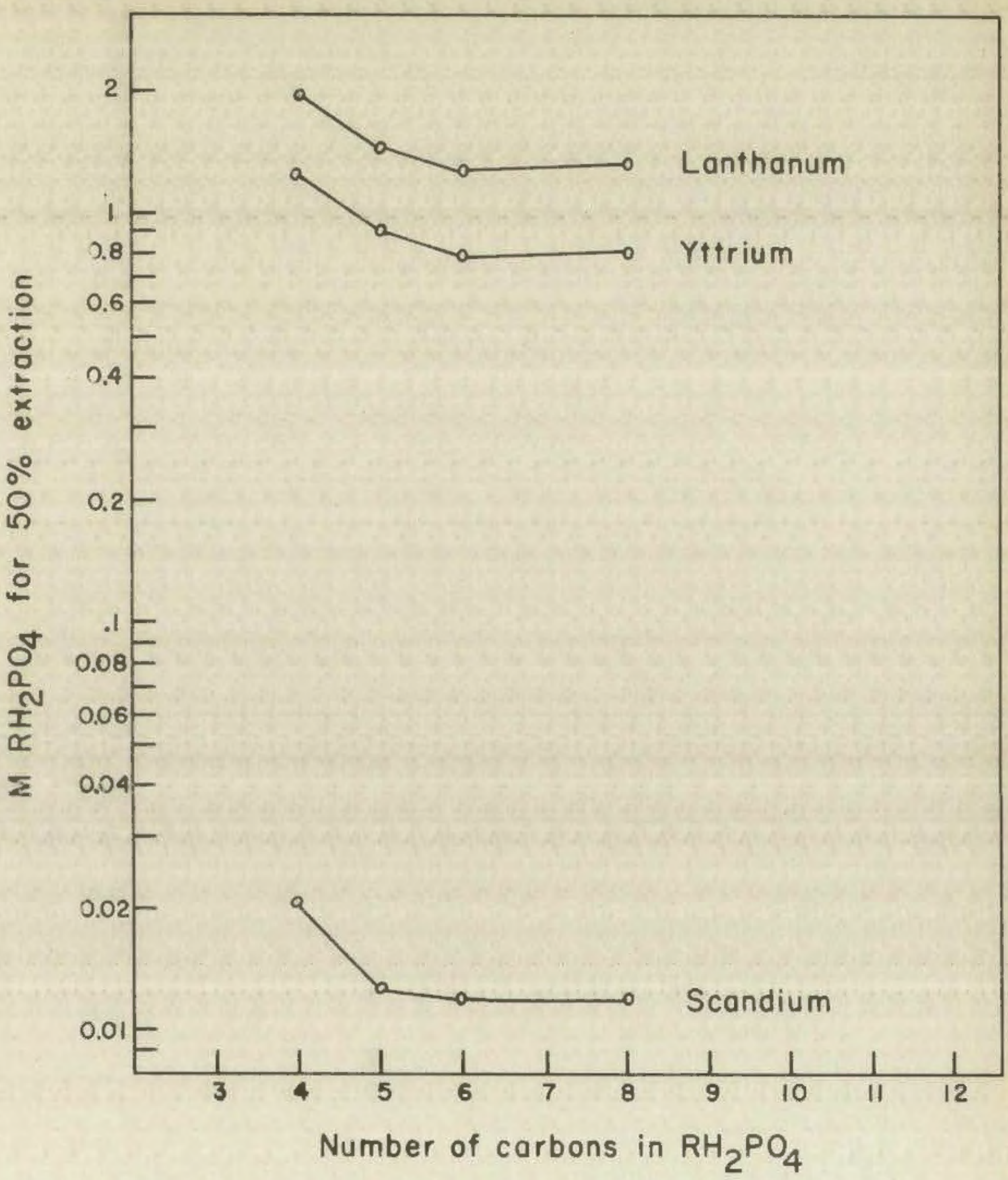

Fig. 27. The dependency of the extraction of lanthanum, yttrium, and scandium on the alkyl group in RH_2PO_4 at 0.274 M HNO_3.

phosphoric acid to extract the metal ions of group IIIa elements. The concentration of the reagent required for 50 percent extraction is a measure of the tendency to form extractable complexes. Lower concentrations of the reagent are required for the compounds which are stronger extracting reagents.

The stability constants of the reactions represented by Equations 22, 23, and 24 were determined for the monoamyl, monohexyl, and monooctyl derivatives of phosphoric acid. These were determined from the acid and reagent concentrations at 50 percent extraction from Figures 15 to 26. The averages of the coefficients from Table XIII were used as the exponents for Equations 25 and 26. The stability constant for scandium is given below.

$$K_{Sc} = D \times \frac{\left[H^{+}\right]_{(w)}^{2.6}}{\left[RH_2PO_4\right]_{(o)}^{2.9}} \qquad \text{Eq. 25}$$

The stability constant for yttrium and lanthanum follows:

$$K_{M} = D \times \frac{\left[H^{+}\right]_{(w)}^{2.85}}{\left[RH_2PO_4\right]_{(o)}^{3.9}} \qquad \text{Eq. 26}$$

The results are given in Table XIV.

TABLE XIV

THE STABILITY CONSTANTS OF THE COMPLEXES OF THE MONOALKYL ORTHOPHOSPHORIC ACIDS AND GROUP IIIa IONS

Compound	pK values for		
	Scandium	Yttrium	Lanthanum
AmH_2PO_4	-3.99	1.46	2.20
$HexH_2PO_4$	-4.09	1.23	2.01
$OctH_2PO_4$	-4.19	1.26	2.07

The logarithm of the separation factor of two metals is obtained by subtraction of the corresponding pK values. The separation factor obtained is valid for acid and reagent concentrations of one regardless of the number of moles of each involved in the reaction.

The separation factor is a measure of the ability of the reagent to separate the metal ions. It may be used in various ways. However, the following idealized case illustrates its meaning. A finite volume of the water phase containing equivalent concentrations of the two metals is equilibrated with an infinitesimal volume of the organic phase. The ratio of the concentrations of the two metal ions in the organic phase is numerically equal to the separation factor. In any practical case the actual separation is much less than the separation factor due to the depletion of the metal ion in the water. The effect of the length of the

carbon chain of the alkyl phosphoric acid on the separation factor is given in Table XV. For all practical purposes the separation factor is independent of the size of the organic group.

It is of interest to compare the separation factor obtained in this work with the one reported by Peppard (9) using HDEHP, di(2-ethyl hexyl) orthophosphoric acid, for yttrium and lanthanum. This reagent is considerably more effective than the monoalkyl phosphoric acids as used in this work in separating these elements. The difference is most striking when the separation factors are expressed as natural numbers. The value obtained in this work is approximately 6, while the reported value of HDEHP is about 10,000 for lanthanum and yttrium.

TABLE XV

THE EFFECT OF THE LENGTH OF THE CARBON CHAIN ON THE SEPARATION FACTOR*

Compound	Log S.F. of Sc and Y	Log S.F. of Y and La
AmH_2PO_4	5.45	0.74
$HexH_2PO_4$	5.41	0.78
$OctH_2PO_4$	5.45	0.81

*The separation factors given for scandium and yttrium are valid only when the nitric acid and alkyl phosphate concentrations are one molar.

VII. SUMMARY

A series of monoalkyl orthophosphoric acids were prepared and were used for solvent extractions of the group IIIa ions. The coefficients of the over-all reaction for the extraction process, the equilibrium constants of this reaction, and the separation factors of the metal ions were determined. Both the stability constants and the separation factors attained limiting values for alkyl phosphoric acids with five or more carbon atoms.

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