DISTRIBUTION STUDIES OF RARE EARTH THIOCYANATES

Thesis for the Degree of Ph. D.

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Robert Walter Berry

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DISTRIBUTION STUDIES OF RARE EARTH THIOCYANATES

By

ROBERT WALTER BERRY

A THESIS

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VITA

The author, Robert Walter Berry, was born on October 27, 1928, in Atlanta, Georgia. He received his elementary and secondary education from the public schools of Atlanta. In 1950, he was graduated with high honor from the Clemson Agricultural College with the degree of Bachelor of Science in Chemistry.

In September of 1950, he entered the School for Graduate Studies at Michigan State College, and was a student there until June of 1951, when he was called to active duty as a second lieutenant in the Chemical Corps of the United States Army. While in the army, the author served as a research physical chemist at the Chemical Corps Chemical and Radiological Laboratories, Army Chemical Center, Maryland. Upon his release from active duty, he returned to Michigan State University.

Mr. Berry is a member of the American Chemical Society, the Society of Sigma Xi, and Sigma Pi Sigma.

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INTRODUCTION

This dissertation is concerned with a study of the solvent extraction properties of the rare earths. Originally, the term "rare earths" was ambiguously used as a term for any metal oxides about which little was known. The designation has ultimately been restricted to elements of the periodic group III-A, scandium through lutetium. Hopkins (27) gives the following definition: "a group of metals, usually trivalent, forming basic oxides, with oxalates insoluble in dilute mineral acids. Their fluorides are also difficultly soluble, hence they may be separated from other elements by adding oxalic or hydrofluoric acid to their solution to which some mineral acid has previously been added. Doubtless the most striking fact which characterized these elements is the remarkable similarity in both the physical and chemical properties of their compounds." From the spectroscopists' point of view, only elements 58 through 70 (cerium through ytterbium) are included as rare earths, because these are the only members which have an electronic structure involving a partially filled 4 - f electron subshell.

Probably the most common use of the term "rare earth group" includes elements 57 through 71 (lanthanum through lutetium), although many authorities include yttrium and scandium because of their similar properties. The terms lanthanides and lantha-

nons have been suggested for the group of elements from atomic number 57 through 71 to correspond to the terms actinides and actinons for the "second rare earth group" (37).

The extreme similarity in properties of rare earth compounds has made the separation of the group into individual elements a most arduous task, and for this reason, most of the work that has been done with this group of elements has been done with their separation in mind.

Various investigators have utilized the techniques of fractional crystallization, fractional sublimation, homogeneous phase precipitation, ion exchange, extraction, and various other methods in order to isolate individual members of the group. Most of these methods are time consuming and require tedious procedures or constant attention. Ion exchange methods have been used extensively in the isolation of pure rare earth compounds, but dilute solutions must be employed, and as yet, commercial applications have been limited. Peppard et al. (46) have used solvent extraction techniques with success, and Weaver (73) has separated one kilogram of gadolinium oxide utilizing Peppard's method.

A volatile compound of the rare earths would be most valuable in that fractional distillation techniques could be utilized. Many investigators have attempted to prepare covalent compounds of the rare earths, in the hope that they might be volatile,

without success. It is doubtful that a truly covalent compound of the rare earths exists.

Solvent extraction methods would be almost ideal for a commercial method of separation, in that a continuous extraction process could be utilized, and a minimum of human labor would be required. Theoretically, any member of the rare earths can be separated from the remainder, in any desired degree of purity, in only two operations. (1, 46)

The requirements for a material which would make it suitable for solvent extraction are that it be soluble in each of the immiscible solvents, that it be stable, and that it be of reasonable cost. Several good reviews have recently been published on solvent extraction in general (1, 68, 69), so no attempt will be made to elaborate on this topic here.

Since the method of liquid-liquid extraction has the advantage of being capable of continuous operation with a minimum of manpower required, it is felt that future advances in the separational methods for the rare earths will probably be in this area. The historical section which follows will present several methods that have been devised for utilizing this technique for the separation of crude mixtures of rare earths, but no study seems to have been made on the nature of the extraction process. It was from this point of view that the study described in this thesis was planned.

HISTORICAL

The earliest use of the principle of distribution in the purification of the rare earths was proposed by Urbain (66) to separate thorium from the precipitated oxalates. Thorium oxalate was redissolved in ammonium oxalate, which also dissolved some cerium. The hydroxides, precipitated by ammonia, were suspended in dilute alcohol and treated with acetylacetone. The thorium acetylacetonate formed was extracted with chloroform, the cerium compound was not dissolved. James (32) adapted the method to remove thorium in his scheme for the separation of the rare earths. P. and G. Urbain (67) used a similar method in the purification of scandium. Scandium hydroxide was precipitated by ammonia in the presence of a slight excess of acetylacetone, and the scandium acetylacetonate was extracted with chloroform. The separation was completed by sublimation in vacuo at 200°, only the scandium acetylacetonate being volatile.

Stoddart and Hill (57) investigated a method of differential extraction, if not a distribution, by treating rare earth stearates with various organic solvents in a Soxhlet extractor. Ether, alcohol, carbon disulfide, and chloroform extracted only the trace of stearic acid present. Benzene caused a slight separation, carbon tetrachloride and xylene did initially, but on further treatment dissolved all the material, as did toluene, molten naphthalene and anthracene, and hot olive oil.

Barneby (5) investigated the solubilities of rare earth compounds in non-aqueous solvents, and their precipitation by adding solutions of inorganic and organic acids. He suggested fractional crystallization of the basic nitrates in acetone instead of water, and noted that the reactions in acetone solution are of the same general order as those in aqueous solution. He made no mention of distribution, however. Schaeffer (53) studied the solubilities of rare earth nitrates in various alcohols, but did not suggest their use for separations.

A distribution method for separating cerium from the other rare earths was proposed by Imre (29), who found that the distribution coefficient of cerium (IV) between water and ether depended on the concentration of cerium, the concentration of nitric acid, and the relative volumes of ether and water. Under the proper conditions, more than 98 percent of the cerium may be removed. Wells (74) measured the solubilities of the nitrates of nine rarer elements in ether. He found difficulties because of uncertainties in hydration, and he mentioned that "ether may find some application in a method of separating the rare earths".

The solubilities of rare earth chlorides in non-aqueous solvents were measured by Hopkins and Quill (28) who suggested extraction of the nitrates with ether as a method of removing small amounts of neodymium present as an impurity in praseodymium.

It remained for Fischer, Seitz, and Jübermann (18) to suggest

fractional distribution between immiscible solvents as a general method for the separation of all the rare earths. They state that the rare earth halides will distribute themselves between water and alcohols, ethers, and ketones, and that by the proper choice of salts and solvents, the difference in distribution coefficients of salts of two rare earths differing in atomic number by one may amount to 50 percent. No data were given to support this statement, and a later review by a member of Fischer's Laboratory, Bock (7), makes no mention of such a large difference in distribution coefficients. It is probable that Fischer was unable to reproduce the previously reported results.

Appleton and Selwood (2) found that the rare earth thiocyanates were soluble in n-butyl achohol, and were able to obtain a partial separation of lanthanum and neodymium by extracting the aqueous thiocyanates with butyl alcohol. The enrichment factor for neodymium was only 1.06, but they expressed hope for the possibility of a continuous extraction process. Leventhal (36) also studied the distribution of rare earth thiocyanates, perchlorates, and nitrates between water and butyl alcohol, but did not believe the method suitable for separation. Asselin, Andrieth, and Comings (3, 4) continued Leventhal's work, and found that thorium was separated from an aqueous solution of thorium and neodymium nitrates by extraction with 1-pentanol containing ammonium thiocyanate.

Templeton (61) worked with rare earth nitrates, utilising

extractions with higher alcohols or ketones, and the extraction of the rare earths was found to increase with atomic number. Templeton and Peterson (65) studied extractions of rare earth nitrates, and in the separation of lanthanum and neodymium by extracting the aqueous solution with n-hexyl alcohol, found the enrichment in neodymium to be about 1.5 for a single stage operation. For a three stage extraction, the enrichment was 2.14. Templeton et al. (49, 63, 64) studied the distribution of thorium nitrate between water and various alcohols and ketones.

Fischer and Bock (17) purified scandium by extracting from aqueous ammonium thiocyanate solution with diethyl ether. Fischer and Chalybaeus (20, 21) report a separation of zirconium and hafnium by means of the extraction of the thiocyanates into diethyl ether. Bock and Bock (8, 9) found that cerium, scandium, and thorium nitrates may be extracted from nitric acid solutions with ether, esters, ketones, and alcohols. They state that more than 95 percent of the cerium is extracted from 8 N nitric acid. Bock and Meyer (10) report the separation of 99.5 percent cerium with yields of 85 percent by extracting the nitrates with diethyl ether. Fischer et al. (19) report fair separation of a crude mixture of the rare earths utilizing the distribution of the rare earth nitrates between aqueous lithium nitrate and either diethyl ether or 2-pentanone, and report extractabilities of the rare earths to increase according to the following series: lanthanum,

cerium, praseodymium, gadolinium, neodymium, yttrium, samarium, dysprosium, holmium, erbium, and lutetium.

Suttle (58, 59) studied the chelation of lanthanum and cerium by thenoyltrifluoroacetone using extraction techniques. Lanthanum and cerium in tracer quantities were extracted with benzene solutions of the chelating agent from aqueous solutions at various pH's. Keenan and Suttle (33) made similar studies with praseodymium. Rydberg (50) studied complex formation of acetylacetone with the actinides by a liquid-liquid distribution technique. Broido (11) found that scandium may be separated from the rare earths in a single extraction with a benzene solution of thenoyltrifluoroacetone at a pH of 1.5. Moeller and Jackson (41) determined the distribution of neodymium and europium by extracting aqueous solutions at high (9.4) pH's with a chloroform solution of 5, 7-dichloro-8-quinolinol. Dyrssen and Dahlberg (14) studied the extraction of lanthanum, samarium, hafnium, thorium, and uranium (IV) nitrate with a chloroform solution of either cupferron or oxine.

Wylie (76) has examined the extraction of cerium (IV) nitrate from 5 - 6 normal nitric acid solutions with ether, and found that as much as 99 percent of the cerium in a rare earth mixture is extracted. He showed that the extracted cerium was present as a mixture of $H_2Ce(NO_3)_6$ and $HCe(NO_3)_5H_2O$. He states that other solvents which extract nitric acid from 5 - 7 normal solutions may be used.

Nagiwara (25) studied the extraction of thorium from aqueous solutions utilising N-nitrosophenylhydroxylamine dissolved in various organic solvents. He used ether, n-butyl acetate, and carbon tetrachloride. The butyl acetate system was studied most extensively.

Warf has proposed the use of tri-n-butyl phosphate (70) and nitromethane (71) for the extraction of cerium (IV) nitrate, but these separations do not appear to be so clean as the ether extraction.

Peppard et al. (46) have recently developed what appears to be a rather promising method for the separation of the rare earths. These workers utilize tri-n-butyl phosphate as the non-aqueous solvent (either pure or diluted with an inert hydrocarbon) and the rare earth nitrates dissolved in concentrated nitric acid as the aqueous phase. Extractability was found to increase with atomic number, but this was reversed in dilute (0.3 M) nitric acid. Scandium could be separated from yttrium and the rare earths in a single operation by using the chlorides instead of the nitrates. Weaver, Kappelmann, and Topp (73) were able to isolate over a kilogram of 95 - 98 percent pure gadolinium oxide by using the method of Peppard. The solutions used by Weaver were: for the feed, 13 normal nitric acid with 20 grams of rare earth oxide per liter; for the aqueous phase, 10 normal nitric acid; and for the organic phase, a 60 percent solution of tri-n-butyl phosphate in

Varsol (a commercial organic petroleum fraction). In a three stage process, the separation factor between gadolinium and terbium was about seven, and between gadolinium and samarium about nineteen. Peppard *et al.* (47) studied the extraction of thorium from pitchblende with tri-n-butyl phosphate, and were able to isolate gram quantities of thorium-230. Peppard, Gray, and Mathus (45) have also studied the extraction of the actinides utilizing the same reagents. Scadden and Ballou (52) were able to separate yttrium from the lanthanum group by an extraction of the solution with a 0.6 molar solution of di-n-butyl phosphoric acid in di-butyl ether.

Schweitzer and Scott (54) determined the extraction of yttrium into acetylacetone from aqueous solutions at various pH's, and Steinbach and Freiser (55, 56) made similar studies for various other metals, but not for the rare earths. Hagemann (24) studied the extraction of actinium salts by a benzene solution of thenoyltrifluoroacetone. Kennelley (34) has studied the extraction of lanthanum, neodymium, and europium acetylacetonates into chloroform from aqueous solution as a function of pH, and found that little difference in their extractabilities exist.

Eberle and Lerner (15) combine the methods of Byrnes and Peppard for an analytical method for the determination of scandium. Their method involves first extracting the aqueous solution with a solution of cupferron in chloroform, precipitating the extracted scandium as tartrate, and then extracting the scandium from this material with tri-n-butyl phosphate from aqueous hydrochloric

acid solution. Lerner and Petretic (35) remove thorium from a rare earth mixture by extracting the bulk of the thorium with dibutoxytetraethyleneglycol, and then the residual thorium is removed by extracting the aqueous solution with a solution of 8-quinolinol in chloroform.

This history shows a complete absence of any study aimed at the nature of the process involved in the distribution of rare earths between aqueous solutions and an organic solvent. The next section should provide the background for the point of view taken in the design of the study presented in this thesis.

THEORETICAL

Irving, Rossotti, and Williams (31) have presented a very general treatment on the solvent extraction of inorganic compounds, and most of the material in this section may be amplified by consulting their paper. Classically, the simplest type of partition between two immiscible liquids is given by the Nernst partition law: $(X)_o = p(X)$, where $(X)_o$ represents the concentration of X in the organic phase, and (X) represents the concentration of X in the aqueous phase. Should X be polymerized in the organic phase to a species X_n, which is not partitioned itself, then $(X_n)_o = K(X)_o^n$. If $(X_n)_o$ is much greater than $(X)_o$, then the distribution ratio, q, is given by the following equation:

$$q = nK(X)_o^n/(X) = nKp(X)^{n-1}.$$

This equation implies that the gradient of a logarithmic plot of q (experimentally determined) versus (X) will give the degree of polymerization of X in the organic phase. Such simplicity is not generally the case for inorganic systems, however. In these systems the actual species which may cross the phase boundary may be only a minor component of a very complex system.

First, let us examine the equilibria existing between the simple ions and all of the various species which may make up the system of two relatively immiscible liquid phases. Step equilib-

ria can be used to describe the concentrations of different species existing in the aqueous phase, and a series of partition coefficients used to relate these concentrations to those in the organic phase.

If we consider an aqueous solution which is in equilibrium with a relatively immiscible organic solvent, S, and contains metal ions, M^{+v}, hydrogen ions, H^{+}, and anions, N^{-z}, and if we assume that hydrolysis of any of the cationic species present is not appreciable, all the complex ions, acido-species, and polynuclear species which might exist in step equilibria can be represented by a general term $H_hM_mN_n(H_2O)_wS_s$, and their concentrations related to those of the simplest ions by a series of overall equilibrium constants defined as follows:

$$k_{hmnws} = (H_hM_mN_n(H_2O)_wS_s)/(H)^h(M)^m(N)^n(H_2O)^w(S)^s, \qquad (1)$$

where h, m, n, w, and s represent the number of hydrogen ions, metal ions, ligand ions, water molecules, and solvent molecules associated with the complex. Partition coefficients for each of the possible species are defined by

$$P_{hmnws} = (H_hM_mN_n(H_2O)_wS_s)_o/(H_hM_mN_n(H_2O)_wS_s), \qquad (2)$$

where the subscript o is used to distinguish the organic phase from the aqueous phase. A general distribution ratio may be written as:

$$q = \frac{\text{total concentration of metal in the organic phase}}{\text{total concentration of metal in the aqueous phase}}$$

$$= \frac{\sum m(H_h M_m N_n (H_2O)_w S_s)_o}{\sum m(H_h M_m N_n (H_2O)_w S_s)}$$

$$= \frac{\sum p_{hmnws} k_{hmnws} m(H)^h (M)^m (N)^n (H_2O)^w (S)^s}{\sum k_{hmnws} m(H)^h (M)^m (N)^n (H_2O)^w (S)^s} , \qquad (3)$$

where the summation includes all physically significant combinations of h, m, n, w, and s. This equation may be simplified by excluding terms from the numerator in which p_{hmnws} is equal to zero. Considerations of electroneutrality require the exclusion of the distribution of charged species, and impose the condition $nv + h = ns$. The average composition of the different species in the aqueous phase may always be represented by a single symbol, viz., $H_{\bar{m}\bar{h}} M_{\bar{m}} N_{\bar{m}\bar{n}} (H_2O)_{\bar{m}\bar{w}} S_{\bar{m}\bar{s}}$, where $\bar{m}$ represents the polymerization number, and $\bar{h}$ and $\bar{n}$ the average number of hydrogen and ligand atoms or ions per atom of metal, and $\bar{w}$ and $\bar{s}$ represent the average number of water molecules and solvent molecules per atom of metal. The above equation (3) may now be written in the form

$$q = \bar{m}(H_{\bar{m}\bar{h}} M_{\bar{m}} N_{\bar{m}\bar{n}} (H_2O)_{\bar{m}\bar{w}} S_{\bar{m}\bar{s}})_o / \bar{m}(H_{\bar{m}\bar{h}} M_{\bar{m}} N_{\bar{m}\bar{n}} (H_2O)_{\bar{m}\bar{w}} S_{\bar{m}\bar{s}})$$

$$= \frac{\bar{p}\bar{m}\bar{k}(H)_o^{\bar{m}\bar{h}} (M)_o^{\bar{m}} (N)_o^{\bar{m}\bar{n}} (H_2O)_o^{\bar{m}\bar{w}} (S)_o^{\bar{m}\bar{s}}}{\bar{m}\bar{k}(H)^{\bar{m}\bar{h}} (M)^{\bar{m}} (N)^{\bar{m}\bar{n}} (H_2O)^{\bar{m}\bar{w}} (S)^{\bar{m}\bar{s}}} . \qquad (4)$$

Expressing equation (4) in logarithmic form, we have

$$\log q = \log(\bar{p}\bar{k}_o/\bar{k}) + \log(\bar{m}_o/\bar{m}) + (\bar{m}_o\bar{h}_o - \bar{m}\bar{h})\log(H)$$
$$+ (\bar{m}_o - \bar{m})\log(M) + (\bar{m}_o\bar{n}_o - \bar{m}\bar{n})\log(N)$$
$$+ (\bar{m}_o\bar{w}_o - \bar{m}\bar{w})\log(H_2O) + (\bar{m}_o\bar{s}_o - \bar{m}\bar{s})\log(S).$$

If the ionic strength is kept constant, and (S) and (H_2O) are kept constant, and provided there is no change either in solvation or in the solvent properties of the two phases, the last two terms of the above equation may be combined with the first term to give

$$\log q = A + \log(m_o/m) + (\bar{m}_o\bar{h}_o - \bar{m}\bar{h})\log(H) + (\bar{m}_o - \bar{m})\log(M) + (\bar{m}_o\bar{n}_o - \bar{m}\bar{n})\log(N), \quad (5)$$

where the term A is independent of (H), (M), and (N), and can be eliminated by differentiation. By partial differentiation, the theoretical meaning of the slope of the logarithmic plot of the extraction coefficient versus the concentration of metal, ligand, or hydrogen ion may be evaluated. The partial differential with respect to the logarithm of free ligand concentration is equal to $(\bar{n}_o\bar{n}_o - \bar{m}\bar{n})$, the partial differential with respect to the logarithm of free metal ion concentration is equal to $(\bar{m}_o - \bar{m})$. The value for the variation with respect to hydrogen ion concentration is comparable to that for the ligand concentration, being $(\bar{n}_o\bar{h}_o - \bar{m}\bar{h})$. These quantities represent the difference in the average number of ligand ions, metal ions, or hydrogen ions associated with the complex in the organic phase and the average number associated with the complex in the aqueous phase.

The experiments described in the next section of this thesis were devised to give the type information necessary to make the kind of analyses described above. The thiocyanates were chosen for study because it was felt that since the thiocyanates of many of the transition metals are extractable from aqueous solutions by

organic solvents, the thiocyanates of the rare earths might also prove to be extracted. Tri-n-butyl phosphate was chosen as the non-aqueous solvent because of the successful use of this solvent for the extraction of rare earth nitrates (46). The concentration ranges were chosen for study from the point of view of usefulness to an industrial process. It was felt that as few variables as possible should be introduced, and for this reason, the effect of dilution of the tri-n-butyl phosphate with an inert hydrocarbon was not studied. With this background, we may now proceed to the experimental section.

EXPERIMENTAL

In order to utilize the theory of Irving et al., the distribution experiments described here were designed so as to learn the effects of the various variables of the system: rare earth concentration, thiocyanate concentration, and the acidity. Experiments were performed in which two of these variables were kept constant, and the third varied. In this way, the effect of each individual variable was measured. In the presentation which follows, the experiments with each rare earth studied are presented together, so all extraction data concerning lanthanum will be found in one section, whereas those concerning neodymium will be found in another, etc.

Purity of Rare Earths Used

Quantitative work on the rare earths often necessitates average atomic weight determinations of the particular samples being used in order to estimate the purity of those samples. The usual method for this determination is to find the oxalate to oxide ratio (16). This cannot be done by the simple ignition of the oxalate, because the rare earth oxalates do not easily become anhydrous. The method usually employed to obtain this ratio is to find the percent oxalate in a sample by titration with standardized permanganate, and the percent rare earth oxide by simple ignition. The average atomic weight is then calculated as follows:

$$2R + 3O = \frac{\frac{\text{wt oxide obtained}}{\text{wt oxalate ignited}} \times \text{wt oxalate titrated} \times 3C_2O_3}{N \text{ of } KMnO_4 \times \text{ml } KMnO_4 \times \text{meq. wt of } C_2O_3}.$$

The rare earths used for this study were all from the Michigan State University stock. The average atomic weight of the lanthanum was 138.9. Freshly ignited lanthanum oxide samples were perfectly white. Tests for cerium were negative, and lanthanum solutions showed no absorption bands for other rare earths.

The neodymium had an average atomic weight of 144.4, and the freshly ignited oxide was pale blue in color. Absorption spectra of the neodymium solutions show but slight absorption in the regions characteristic for both praseodymium and samarium. The amount of these two rare earths present, however, was insufficient to affect the measurements made using this material. The absorption spectrum of the neodymium used is shown as Figure 1. The spectrum was taken on a Beckman model D.K.-2 recording spectrophotometer using a one centimeter cell, and a solution 0.15 formal with respect to neodymium. Tests for cerium were negative.

The praseodymium material had been purchased from the Lindsay Chemical Company and was coded as the 99.8 percent praseodymium oxide (Lindsay Code 729). This material was black in color, and a perchlorate solution gave an absorption spectrum which had no absorption bands for other rare earths. The absorption spectrum for the praseodymium used is shown as Figure 2. The spectrum was taken through a one centimeter cell, using a solution 0.18 formal with respect to praseodymium.

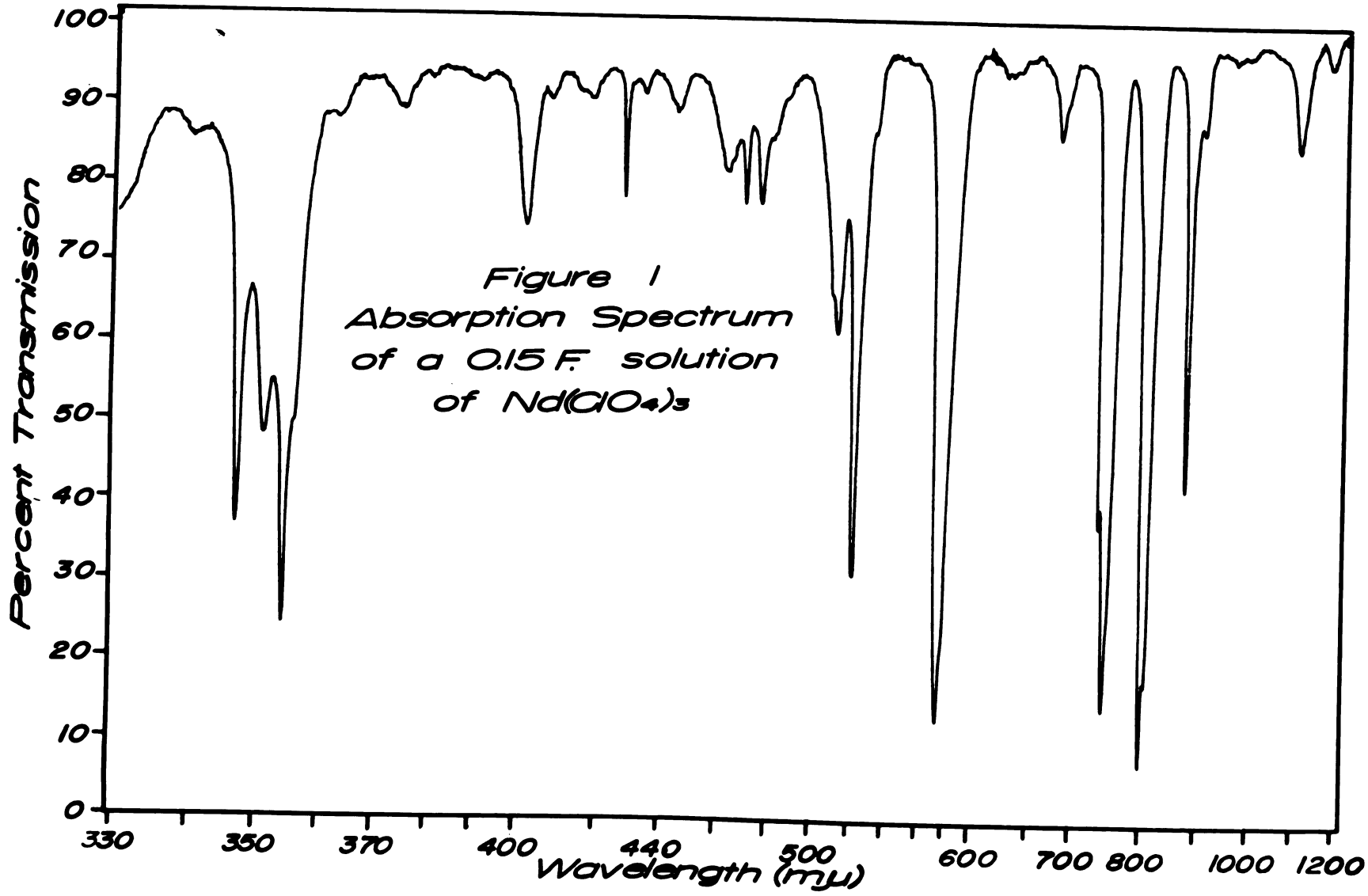

Figure 1
Absorption Spectrum
of a 0.15 F. solution
of $Nd(ClO_4)_3$

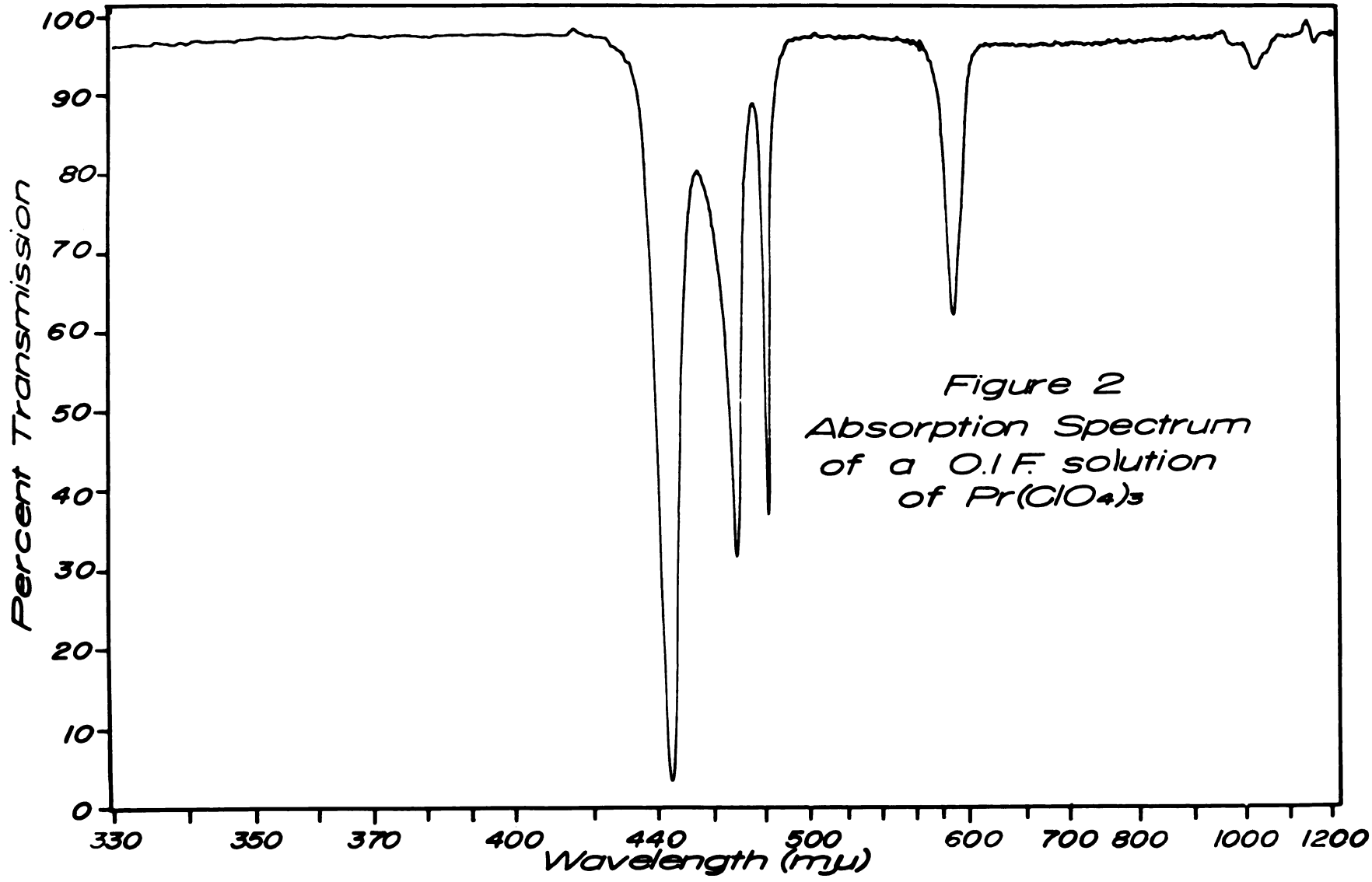

Figure 2
Absorption Spectrum
of a 0.1 F. solution
of $Pr(ClO_4)_3$

The freshly ignited samarium oxide was pale cream in color. The absorption spectrum showed no absorption bands for other rare earths. The absorption spectrum of the samarium used is shown as Figure 3. The spectrum was taken through a one centimeter cell, using a solution 0.2 formal with respect to samarium.

Rare Earth Thiocyanates

The rare earth thiocyanates were prepared by the metathetical reaction of barium thiocyanate and rare earth sulfate. The procedures were essentially the same in all cases, except that in one case crystals of the compound were prepared, and in the remainder, the solution was used as such. The procedures for each case are described later.

Neodymium Thiocyanate

The preparation of neodymium thiocyanate in crystalline form started with sixty-five grams of neodymium oxide dissolved in thirty-five milliliters of concentrated sulfuric acid which had been previously diluted to about 750 milliliters. In order to dissolve all of the neodymium sulfate, this solution had to be diluted again to a volume of approximately four liters. The solution was then filtered. One hundred sixty-five grams of barium thiocyanate was dissolved in about 750 milliliters of water, and both this solution and the neodymium sulfate solution were heated to almost boiling. The barium thiocyanate was then added slowly to the neodymium sulfate solution, and this was then allowed to

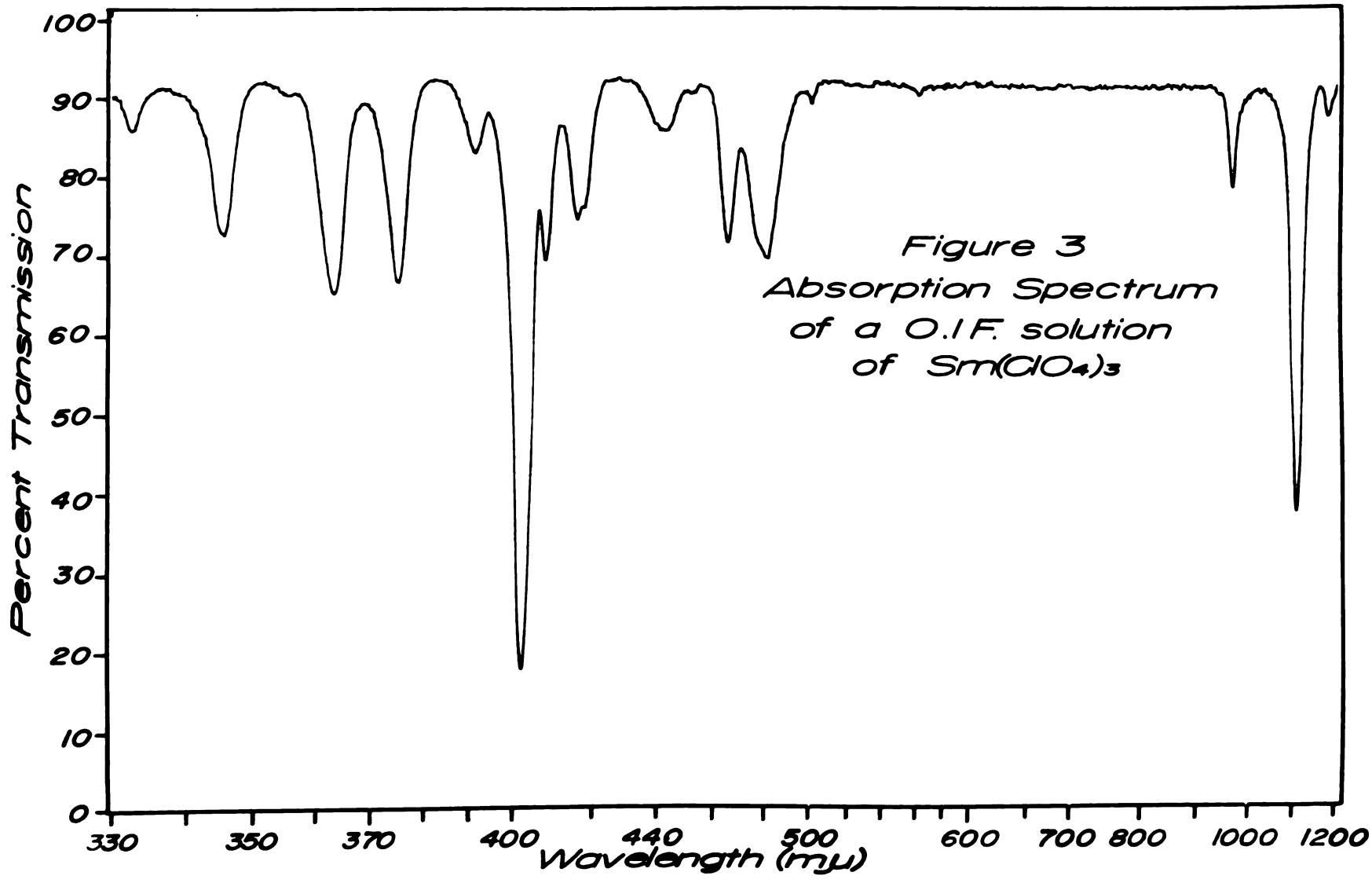

Figure 3
Absorption Spectrum
of a 0.1 F. solution
of $Sm(ClO_4)_3$

cool. The barium sulfate formed was removed by filtration, and the filtrate evaporated to a volume of approximately one liter on a steam bath. It was further evaporated by placing the solution in a crystallizing dish, and placing this in a desiccator over concentrated sulfuric acid, and the desiccator evacuated. Not until the volume of the solution had reached about 125 milliliters did any crystals begin to appear. Evaporation was continued until a fair amount of crystalline neodymium thiocyanate had formed. This material was collected by filtering, and the crystals were taken up in 250 milliliters of conductivity water. This solution was then analyzed for neodymium and the formality was found to be 0.572 with respect to neodymium. The solution was analyzed as follows: twenty-five milliliters of the solution was diluted to 250 milliliters, and twenty milliliter samples of this solution were placed in 250 milliliter beakers, diluted to about 100 milliliters, acidified, and heated to almost boiling. Hot oxalic acid was then added to precipitate the neodymium as neodymium oxalate. The neodymium oxalate was collected on Carl Schleicher and Schuell white ribbon filter paper, dried, and ignited at 975°C. in platinum crucibles. The analytical data are given as Table I.

Table I

Analysis of $Nd(SCN)_3$ Solution for Neodymium

Weight Nd_2O_3	Formality
0.1920	0.5711
0.1924	0.5723
0.1926	0.5729

The thiocyanate content was analyzed by titrating two milliliter samples of the stock solution with 0.100 N. silver nitrate solution, using eosin as indicator. The formality of the solution with respect to thiocyanate was 1.51. The analytical data for this determination are given as Table II.

Table II

Analysis of $Nd(SCN)_3$ Solution for Thiocyanate

Ml. $AgNO_3$	Formality
30.30	1.515
30.20	1.510
30.20	1.510

Lanthanum Thiocyanate

Lanthanum thiocyanate was prepared by essentially the same method as was used for the neodymium salt, except that more care was used in the weighing of the lanthanum oxide and the barium thiocyanate, and in the measurement of the amount of sulfuric acid used. The solution remaining after the barium sulfate was removed was not evaporated to crystals, but only taken down to

a volume of approximately one liter. The solution was analyzed by the method described for neodymium, except that it was necessary to digest the precipitated lanthanum oxalate over a hot plate for a period of about two hours in order to coagulate the precipitate, and simplify the filtration. The analytical results are listed as Table III.

Table III

Analysis of $La(SCN)_3$ Solution for Lanthanum

Weight La_2O_3	Formality
0.0737	0.4524
0.0744	0.4567
0.0744	0.4567

The solution was analyzed for thiocyanate by taking five milliliter samples of a solution made to be 0.205 formal in lanthanum, and adding silver nitrate solution. The silver thiocyanate precipitate was digested on a hot plate for about two hours, allowed to cool, and then collected in weighed pyrex fritted type gooch crucibles. The formality of thiocyanate which should be present would be 0.615, the formality obtained by analysis was 0.6138, which is a reasonable check for the theoretical amount that should be present. The analytical results are given as Table IV.

Table IV

Analysis of $La(SCN)_3$ Solution for Thiocyanate

Weight AgSCN	Formality
0.5092	0.6136
0.5095	0.6140

Praseodymium Thiocyanate

Praseodymium thiocyanate was prepared by dissolving praseodymium oxide in sulfuric acid, allowing the praseodymium sulfate to crystallize, filtering off the mother liquor, and taking up the crystals in conductivity water. This solution was then analyzed for praseodymium by the same method as described for neodymium. A barium thiocyanate solution was made from C. P. grade barium thiocyanate which had first been recrystallized from absolute methanol. This solution was analyzed by titrating with standard silver nitrate solution, using ferric nitrate as the indicator. Equivalent amounts of the praseodymium sulfate solution and the barium thiocyanate solution were added to one another, and digested for approximately four hours on a hot plate. The precipitated barium sulfate was removed by passing the solution through a fine frit, and the filtrate was evaporated to a volume of approximately 250 milliliters. This solution was then analyzed for praseodymium as described before. The solution was found to be 0.2844 formal with respect to praseodymium. Praseodymium perchlorate was prepared by sprinkling praseodymium oxide into perchloric acid, and stirring over night. The excess praseodymium oxide was filtered

off, and the pH of the solution was measured and found to be about 4.5. This value for the pH is on the acid side of equilibrium, and thus insures a minimum of basic praseodymium salts, and also a minimum of excess perchloric acid.

Samarium Thiocyanate

Samarium thiocyanate was prepared by the same method as described for the praseodymium compound. The solution was analyzed for samarium by the same mehted as was described for the analysis of neodymium thiocyanate, and the solution was found to be 0.325 formal with respect to samarium.

Extraction of Rare Earth Thiocyanates by Tri-n-butyl Phosphate

The solutions described below were made by adding the proper amount of the stock rare earth thiocyanate solution, standard perchloric acid solution to adjust the acidity to the desired value, either ammonium or sodium thiocyanate solution to adjust the thiocyanate concentration, and conductivity water to bring the total aqueous volume to the desired value. (For the exact contents of each solution, see appendix). A volume of tri-n-butyl phosphate equal to the total aqueous volume was added, the container shaken, and the phases allowed to separate. In order to assure equilibrium conditions, the two phases were allowed to remain in contact for at least sixteen hours. The tri-n-

butyl phosphate used was purchased from the Commercial Solvents Company, and before use it was washed with sodium carbonate solution to remove any mono- or di-butyl phosphoric acid which might be present, and then washed ten times with conductivity water. The solutions were analyzed by taking samples from each phase, adding about 75 milliliters of water, heating to almost boiling, and adding hot oxalic acid. The solutions were then allowed to cool. The rare earth oxalate was collected on Carl Schleicher and Schuell white ribbon filter paper, and in the case of the organic phase, it was necessary to wash the filter paper at least three times with methanol or acetone in order to remove all the tri-n-butyl phosphate. Usually, the precipitate was washed twice with methanol and then twice with acetone, dried, and then ignited in platinum crucibles at 975° C. It should be noted that when platinum ware is used at these temperatures for long periods of time the crucibles lose some weight, and it is necessary to weigh the crucible after removing the oxide by washing with dilute hydrochloric acid to obtain the tare weight.

Extraction of Neodymium Thiocyanate

The effect of varying the acidity of the initial solution was studied by determining the distribution coefficients of neodymium thiocyanate at different initial acidities, while the neodymium thiocyanate concentration was held constant at a formality of 0.100. Table V presents the results of these extractions.

Table V

Extraction Data for Neodymium

Run No.	Concentration in Moles per Liter				q
	Nd Original	Acidity Original	Nd Aqueous	Nd Organic	
1	0.100	0.101	0.0545	0.0417	0.876
2	0.100	0.504	0.0773	0.0270	0.312
3	0.100	1.009	0.1028	0.0124	0.120

It may be seen from these results that the distribution coefficients decrease as the initial acidity is increased, or that the distribution coefficient has an inverse dependence on the initial acidity.

The effect of changing the thiocyanate concentration was studied by varying the amount of thiocyanate while the concentration of neodymium and the acidity were held constant. In order to adjust the thiocyanate concentration to the desired values, standardized ammonium thiocyanate solution was added to the mixture of neodymium thiocyanate and perchloric acid. The total volume of the aqueous solution was adjusted to twenty milliliters by adding the proper amount of conductivity water. Twenty milliliters of tri-n-butyl phosphate was then added, and the containers were shaken and the phases allowed to separate. Five milliliter samples were removed from each phase and analyzed for neodymium as described above. The results of these analyses are presented as Table VI.

Table VI

Extraction Data for Neodymium

Run No.	Concentration in Moles per Liter					q
	Nd Original	Acidity Original	SCN Original	Nd Aqueous	Nd Organic	
5	0.100	0.101	0.273	0.0541	0.0499	0.921
6	0.100	0.101	0.308	0.0477	0.0558	1.17
7	0.100	0.101	0.353	0.0412	0.0619	1.50
8	0.100	0.101	0.709	0.0102	0.0927	9.06
9	0.100	0.101	0.442	0.0280	0.0757	2.71
10	0.100	0.101	0.531	0.0190	0.0832	4.37
11	0.100	0.101	0.620	0.0138	0.0927	6.46

It may be seen from these data that the distribution coefficient increases with an increase in the initial thiocyanate concentration. It may be observed then, that the distribution of neodymium thiocyanate between water and tri-n-butyl phosphate is dependent upon the concentration of thiocyanate present in the aqueous phase.

In order to learn whether there was any appreciable dimerization or association in either phase, the effect of the concentration of neodymium on the the distribution was studied. In order to study this effect, extractions were made at two other initial neodymium concentrations. The procedure was the same as before, except that the volume of each phase was increased to forty milliliters so that ten milliliter samples could be taken for analysis. The results of these extractions are presented as Table VII.

Table VII

Extraction Data for Neodymium

Run No.	Concentration in Moles per Liter: Nd Original	Acidity Original	SCN Original	Nd Aqueous	Nd Organic	q
12	0.0715	0.101	0.189	0.0453	0.0286	0.631
13	0.0715	0.101	0.223	0.0383	0.0345	0.902
14	0.0715	0.101	0.278	0.0315	0.0408	1.29
15	0.0715	0.101	0.367	0.0206	0.0506	2.45
16	0.0715	0.101	0.456	0.0140	0.0572	4.07
17	0.0715	0.101	0.545	0.0086	0.0613	7.11
18	0.0715	0.101	0.634	0.0058	0.0631	10.8
19	0.0429	0.101	0.113	0.0329	0.0110	0.335
20	0.0429	0.101	0.157	0.0269	0.0167	0.622
21	0.0429	0.101	0 202	0.0215	0.0219	1.02
22	0.0429	0.101	0.246	0.0162	0.0267	1.65
23	0.0429	0.101	0.291	0.0127	0.0306	2.41

These data indicate that for equal initial acidity and thiocyanate concentration, the distribution coefficient increases with decreasing neodymium concentration. The data presented in Tables VI and VII are presented graphically as Figure 4.

While performing experiments with lanthanum (see below), it was observed that ammonium thiocyanate was extracted into tri-n-butyl phosphate to a greater extent than was the sodium salt. It was also observed that lanthanum perchlorate was extracted even when there was no thiocyanate present. Another series using neodymium was studied with an attempt at controlling the ionic strength made, and in which the thiocyanate concentration was adjusted with standard sodium thiocyanate solution. The results of this series of extractions are given as Table VIII, and presented graphically as Figures 5 and 6.

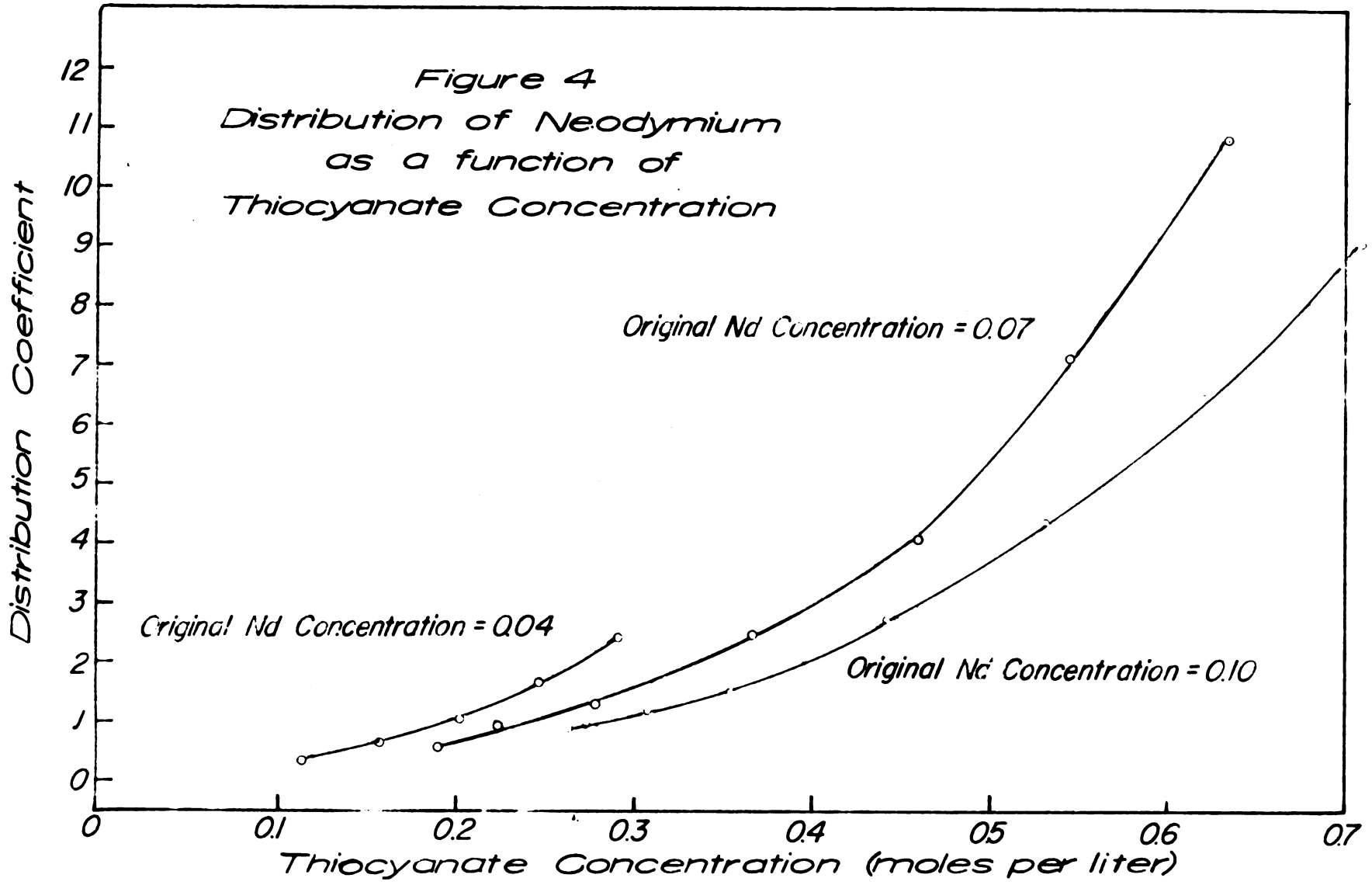
Figure 4
Distribution of Neodymium
as a function of
Thiocyanate Concentration
Distribution Coefficient
Thiocyanate Concentration (moles per liter)
Original Nd Concentration = 0.07
Original Nd Concentration = 0.04
Original Nd Concentration = 0.10
0
1
2
3
4
5
6
7
8
9
10
11
12
0.1
0.2
0.3
0.4
0.5
0.6
0.7

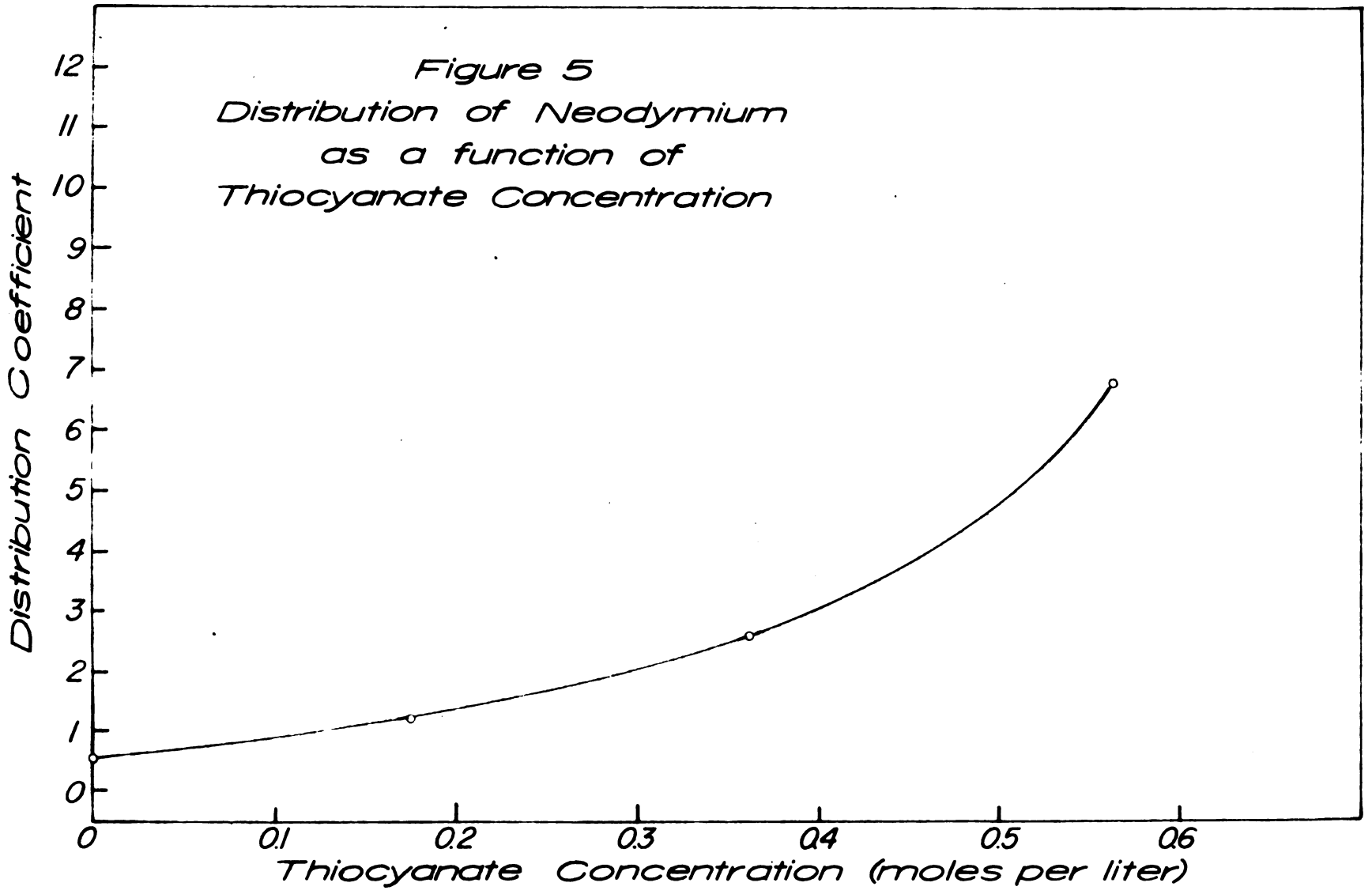
Figure 5
Distribution of Neodymium
as a function of
Thiocyanate Concentration
Distribution Coefficient
12
11
10
9
8
7
6
5
4
3
2
1
0
0
0.1
0.2
0.3
0.4
0.5
0.6
Thiocyanate Concentration (moles per liter)

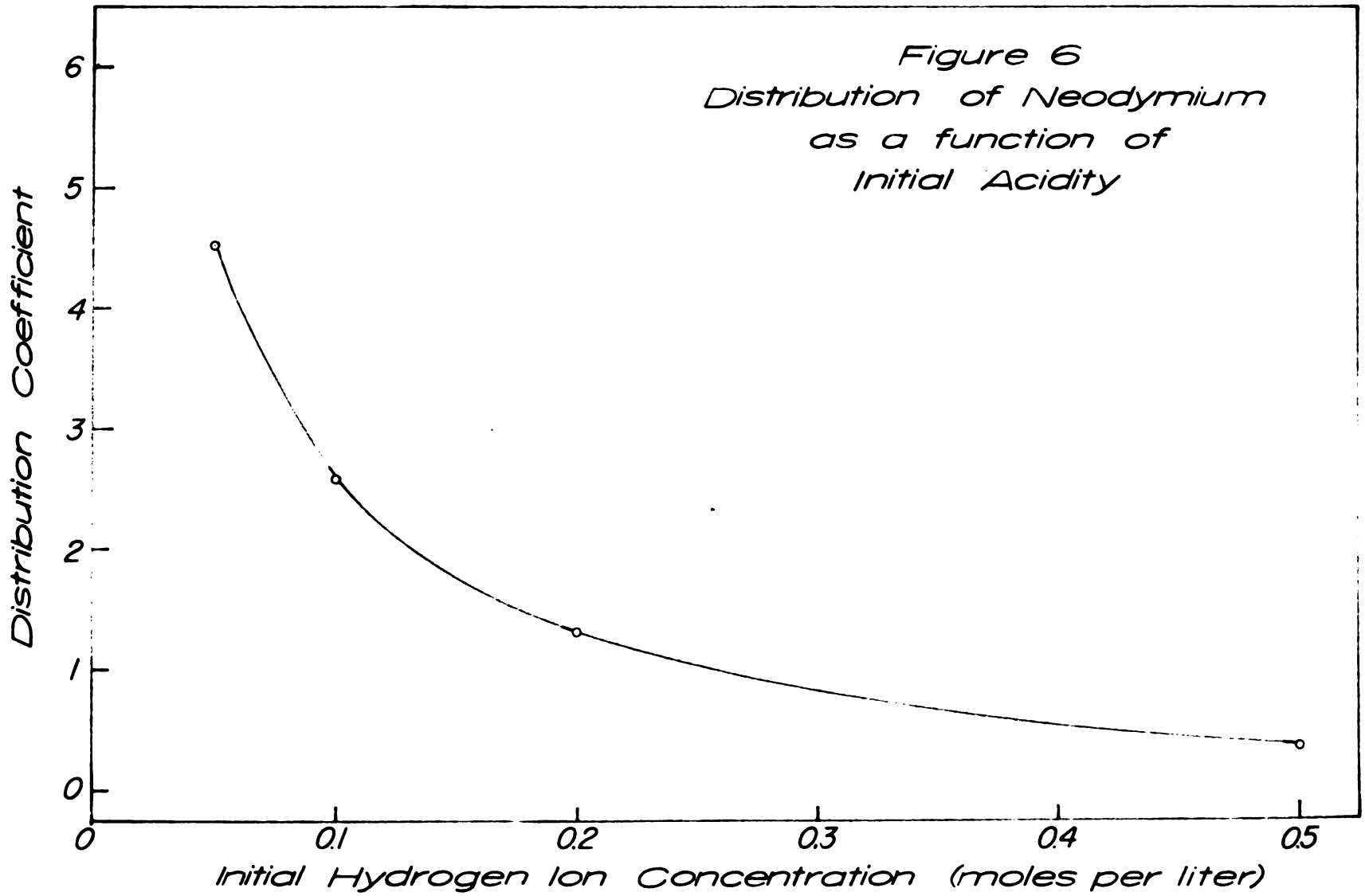
Figure 6
Distribution of Neodymium
as a function of
Initial Acidity
Distribution Coefficient
6
5
4
3
2
1
0
0
0.1
0.2
0.3
0.4
0.5
Initial Hydrogen Ion Concentration (moles per liter)

Table VIII

Extraction Data for Neodymium

Run No.	Concentration in Moles per Liter					
	Nd Original	Acidity Original	SCN Original	Nd Aqueous	Nd Organic	q
24	0.103	0.101	0.000	0.0667	0.0360	0.540
25	0.103	0.101	0.175	0.0469	0.0558	1.19
26	0.103	0.101	0.362	0.0287	0.0740	2.58
27	0.103	0.101	0.562	0.0133	0.0894	6.72
28	0.103	0.050	0.362	0.0186	0.0841	4.52
29	0.103	0.202	0.362	0.0443	0.0584	1.32
30	0.103	0.504	0.362	0.0786	0.0278	0.354

Extraction of Lanthanum Thiocyanate

Lanthanum solutions were prepared in the manner described above, the total aqueous volumes being twenty milliliters for the 0.1 and 0.14 formal solutions, and forty milliliters for the 0.07 and 0.04 formal solutions. The analyses were performed as described above, except that the precipitated oxalate was allowed to digest for approximately two hours before the solutions were removed from the hot plate and allowed to cool. The ignition of the oxalate was done in platinum crucibles at 975° C. or above. The results are similar to those for the neodymium solutions. For the 0.14 formal lanthanum series, lanthanum perchlorate was used in place of the lanthanum thiocyanate, and all the thiocyanate present was added in the form of ammonium thiocyanate. The lanthanum perchlorate solution was prepared by adding an excess of lanthanum oxide to perchloric acid, stirring over night, and removing any remaining oxide by filtration. The pH of the resulting solution was measured and found to be about five. This value

for the pH insured that very little of the lanthanum was present in the form of basic salts, since it is on the acid side of equilibrium, and also represents a minimum excess of perchloric acid. The solution was then analyzed for lanthanum by the method previously described and was found to be 0.2788 formal. The data for a number of lanthanum extractions in which the metal concentration was held constant while the thiocyanate concentration was varied are presented in Table IX. (Note that four different lanthanum concentrations were studied.)

With the exception of the 0.14 formal lanthanum data, these results are quite similar to those for the neodymium. Additional experiments were performed (see below) to explain the variation of the 0.14 formal solution from the values of the others. The data presented in this table are represented graphically in Figures 7 and 8.

Table IX

Extraction Data for Lanthanum

Run No.	Concentration in Moles per Liter of La Original	Acidity Original	SCN Original	La Aqueous	La Organic	q
1	0.103	0.101	0.308	0.0549	0.0498	0.908
2	0.103	0.101	0.397	0.0410	0.0632	1.54
3	0.103	0.101	0.486	0.0284	0.0724	2.55
4	0.103	0.101	0.575	0.0216	0.0805	3.72
5	0.103	0.101	0.664	0.0169	0.0858	5.10
6	0.103	0.101	0.753	0.0131	0.0902	6.87
7	0.0685	0.101	0.205	0.0440	0.0254	0.578
8	0.0685	0.101	0.277	0.0337	0.0355	1.06
9	0.0685	0.101	0.339	0.0260	0.0426	1.64
10	0.0685	0.101	0.428	0.0179	0.0506	2.83
11	0.0685	0.101	0.517	0.0122	0.0560	4.61
12	0.0400	0.101	0.120	0.0312	0.0093	0.299
13	0.0400	0.101	0.191	0.0231	0.0173	0.750
*14	0.0400	0.101	0.298	0.0102	0.0198	1.93
15	0.0400	0.101	0.387	0.0084	0.0315	3.77
16	0.0400	0.101	0.520	0.0042	0.0356	8.41
**17	0.139	0.101	0.205	0.0673	0.0734	1.09
**18	0.139	0.101	0.303	0.0559	0.0836	1.50
**19	0.139	0.101	0.400	0.0459	0.0926	2.06
**20	0.139	0.101	0.498	0.0381	0.1017	2.67
**21	0.139	0.101	0.605	0.0297	0.1094	3.68

* An error was made in the addition of tri-n-butyl phosphate, in that for this extraction 60 milliliters was added instead of the 40 used for the remainder of the solutions.

** For these solutions, all the thiocyanate was added in the form of ammonium thiocyanate, and the lanthanum was added in the form of lanthanum perchlorate.

The thiocyanate concentration for runs one through five, nine, and eleven were determined by precipitating the thiocyanate with silver nitrate solution, and weighing the precipitate. The con-

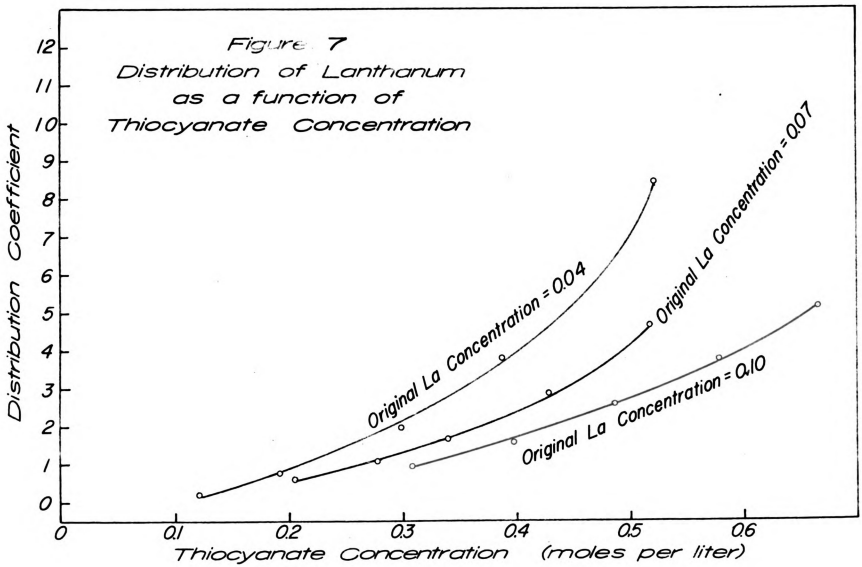
Figure 7
Distribution of Lanthanum
as a function of
Thiocyanate Concentration
Distribution Coefficient
0
1
2
3
4
5
6
7
8
9
10
11
12
0
0.1
0.2
0.3
0.4
0.5
0.6
Thiocyanate Concentration (moles per liter)
Original La Concentration = 0.04
Original La Concentration = 0.07
Original La Concentration = 0.10

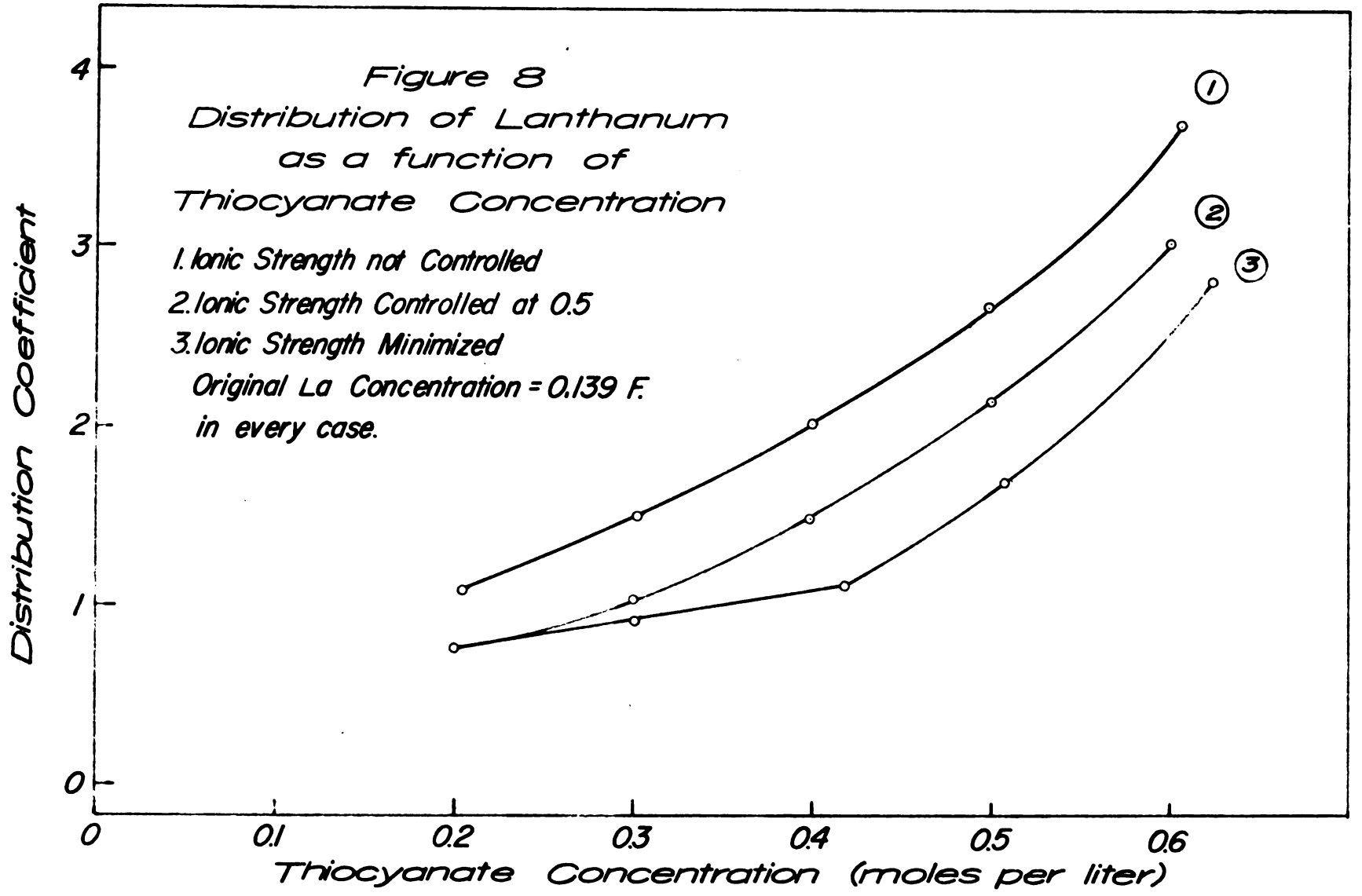
Figure 8
Distribution of Lanthanum
as a function of
Thiocyanate Concentration
1. Ionic Strength not Controlled
2. Ionic Strength Controlled at 0.5
3. Ionic Strength Minimized
Original La Concentration = 0.139 F.
in every case.
Distribution Coefficient
Thiocyanate Concentration (moles per liter)
0
1
2
3
4
0
0.1
0.2
0.3
0.4
0.5
0.6
1
2
3

centrations obtained are given as Table X.

Table X

Extraction data for SCN from $La(SCN)_3$

Run No.	Concentration in Moles per Liter SCN Original	SCN Aqueous	SCN Organic	Organic La/SCN Ratio
1	0.308	0.1082	0.1967	3.95
2	0.397	0.1467	0.2442	3.86
3	0.486	0.1982	0.2854	3.95
4	0.575	0.2445	0.3276	4.07
5	0.664	0.3025	0.3583	4.18
9	0.339		0.1985	4.66
11	0.517		0.2649	4.73

An examination of these data gives the impression that the thiocyanate to rare earth ratio in the organic phase is probably four.

An examination of the data for the 0.139 formal lanthanum solutions indicate that the ionic strength of the solutions plays a not unimportant role in the extractions. It would seem that if one could control the ionic strength of the water solution after extraction to some constant value, the results would be more nearly comparable. For this purpose, several more runs were made in an attempt to control the ionic strength. This necessitated some perhaps rather drastic assumptions. These assumptions are: first, that everything is totally ionized in the aqueous phase, and second, that since it appears that four thiocyanate ions cross the phase boundary for each lanthanum (see Table X), the

decrease in ionic strength from that of the original solution would be seven times the concentration of lanthanum in the organic phase. Using these assumptions, the "ionic strength" of the aqueous phase after extraction can be calculated. The next series of experiments were performed as previously described, except that the distribution coefficients were estimated and the ionic strength of the original solution was calculated to give a final ionic strength of approximately 0.5. If the resulting distribution coefficient was quite different from that estimated, another estimate was made, and the experiment repeated. The results of these experiments are given as Table XI, and presented graphically as Figures 8 and 9.

These data are a further indication of the importance of the ionic strength on the distribution of the rare earths, and they also indicate that the discrepancy in the 0.14 formal lanthanum data previously reported was because of ionic strength differences.

Table XI

Extraction data for Lanthanum

Run No.	Concentration in Moles per Liter of La Original	Acidity Original	SCN Original	La Aqueous	La Organic	u Original	u Final	q
22	0.139	0.101	0.201	0.0780	0.0620	0.937	0.503	0.795
23	0.139	0.101	0.301	0.0730	0.0665	0.937	0.472	0.911
24	0.139	0.101	0.418	0.0652	0.0727	0.937	0.428	1.12
25	0.139	0.101	0.507	0.0514	0.0869	1.026	0.418	1.69
26	0.139	0.101	0.623	0.0361	0.1014	1.14	0.432	2.81
27	0.139	0.101	0.301	0.0689	0.0708	0.992	0.497	1.03
28	0.139	0.101	0.399	0.0566	0.0825	1.064	0.487	1.46
29	0.139	0.101	0.500	0.0437	0.0938	1.147	0.490	2.15
30	0.139	0.101	0.600	0.0341	0.1034	1.237	0.513	3.03
31	0.103	0.101	0.200	0.0503	0.0530	0.851	0.480	1.05
32	0.103	0.101	0.300	0.0401	0.0625	0.917	0.480	1.56
33	0.103	0.101	0.400	0.0359	0.0672	0.983	0.513	1.87
34	0.103	0.101	0.500	0.0238	0.0782	1.041	0.493	3.28
35	0.103	0.101	0.600	0.0187	0.0834	1.081	0.497	4.47
36	0.103	0.101	0	0.0674	0.0344	0.716	0.475	0.51
37	0.0685	0.101	0.400	0.0134	0.0529	0.865	0.495	3.94
38	0.0685	0.101	0.500	0.0105	0.0580	0.896	0.490	5.53
39	0.0685	0.101	0.593	0.0080	0.0604	0.915	0.496	7.57

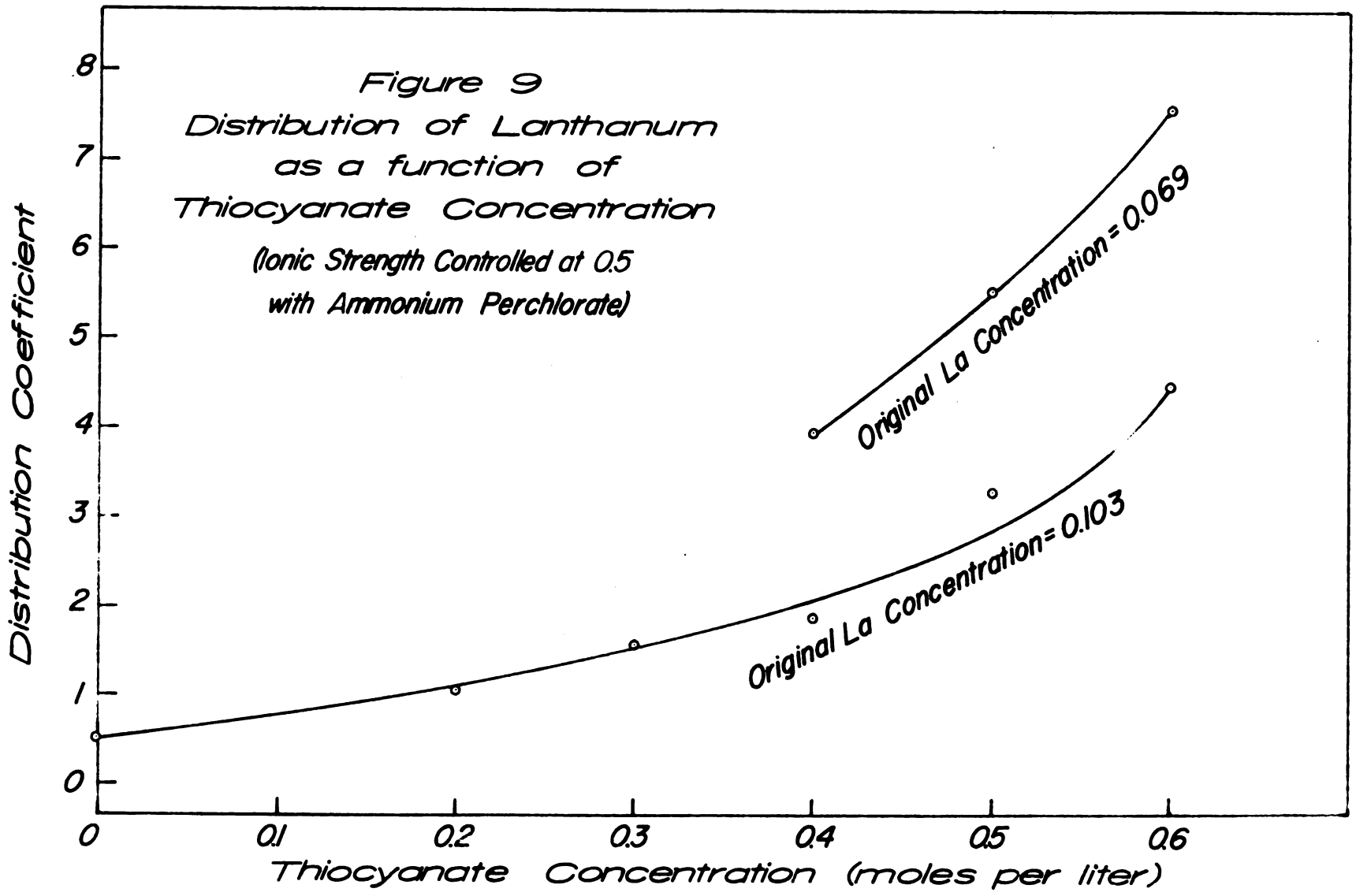
Figure 9
Distribution of Lanthanum
as a function of
Thiocyanate Concentration
(Ionic Strength Controlled at 0.5
with Ammonium Perchlorate)
Distribution Coefficient
0
1
2
3
4
5
6
7
8
0
0.1
0.2
0.3
0.4
0.5
0.6
Thiocyanate Concentration (moles per liter)
Original La Concentration = 0.069
Original La Concentration = 0.103

In order to adjust the ionic strength of the 0.07 formal solutions, some ammonium perchlorate or sodium perchlorate would be necessary in addition to the other salts. It was decided to use the sodium salt for the complete series, and also to use sodium thiocyanate instead of the ammonium salt in order to reduce any hydrolysis effects to a minimum. The 0.4, 0.5, and 0.6 formal thiocyanate solution was run with both the ammonium salt (run numbers 37, 38, and 39) and the sodium salt (run numbers 42, 43, and 44). The data for these solutions, as well as re-runs using sodium salts for the 0.1 and 0.14 formal lanthanum are presented as Table XII, and given in graphical form in Figure 10. Included in Table XII are data from a series of extractions made from 0.1 formal lanthanum solutions, with the thiocyanate concentration held at 0.400 formal, but with varying initial acidities. These data are presented graphically as Figure 11. The data presented here indicate that the effects of the acidity, lanthanum concentration, and thiocyanate concentration are of the same order as was found for neodymium.

Table XII

Extraction Data for Lanthanum

Run No.	Concentration in Moles per Liter of La Original	Acidity Original	SCN Original	La Aqueous	La Organic	q
40	0.0685	0.101	0.200	0.0207	0.0481	2.32
41	0.0685	0.101	0.300	0.0152	0.0535	3.51
42	0.0685	0.101	0.400	0.0109	0.0579	5.30
43	0.0685	0.101	0.498	0.0076	0.0610	8.02
44	0.0685	0.101	0.600	0.0053	0.0632	11.84
45	0.103	0.101	0.200	0.0413	0.0614	1.49
46	0.103	0.101	0.400	0.0283	0.0744	2.63
47	0.103	0.101	0.500	0.0174	0.0853	4.90
48	0.139	0.101	0.200	0.0782	0.0612	0.783
49	0.139	0.101	0.400	0.0525	0.0869	1.66
50	0.139	0.101	0.600	0.0284	0.1110	3.91
51	0.103	0.050	0.400	0.0214	0.0813	3.80
52	0.103	0.101	0.400	0.0283	0.0744	2.63
53	0.103	0.202	0.400	0.0451	0.0576	1.28
54	0.103	0.504	0.400	0.0759	0.0268	0.353

The concentrations of thiocyanate in the organic phase were determined for runs 46, 47, 49, 51,53, and 54 by precipitating the thiocyanate with silver nitrate solution, and weighing the precipitated silver thiocyanate. The values obtained are given as Table XIII.

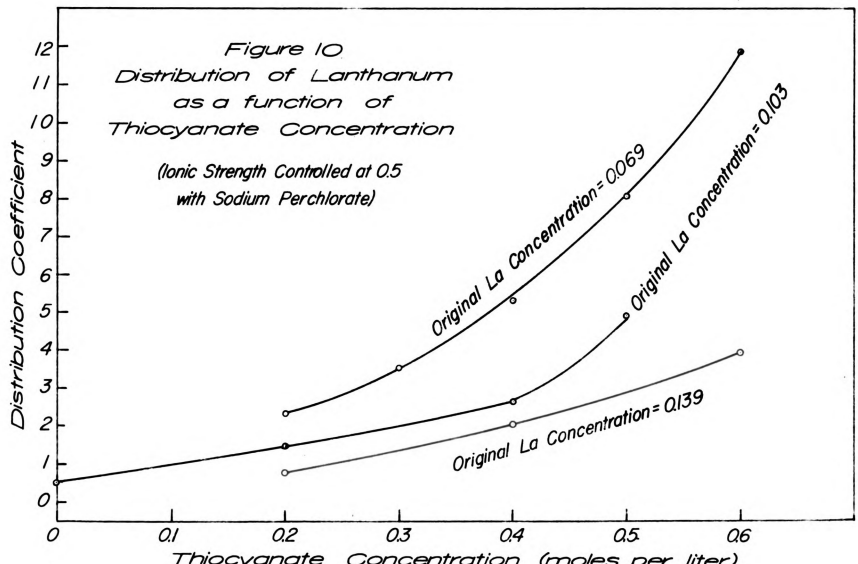
Figure 10
Distribution of Lanthanum as a function of Thiocyanate Concentration
(Ionic Strength Controlled at 0.5 with Sodium Perchlorate)
Original La Concentration = 0.069
Original La Concentration = 0.103
Original La Concentration = 0.139
Distribution Coefficient
Thiocyanate Concentration (moles per liter)
0
1
2
3
4
5
6
7
8
9
10
11
12
0
0.1
0.2
0.3
0.4
0.5
0.6

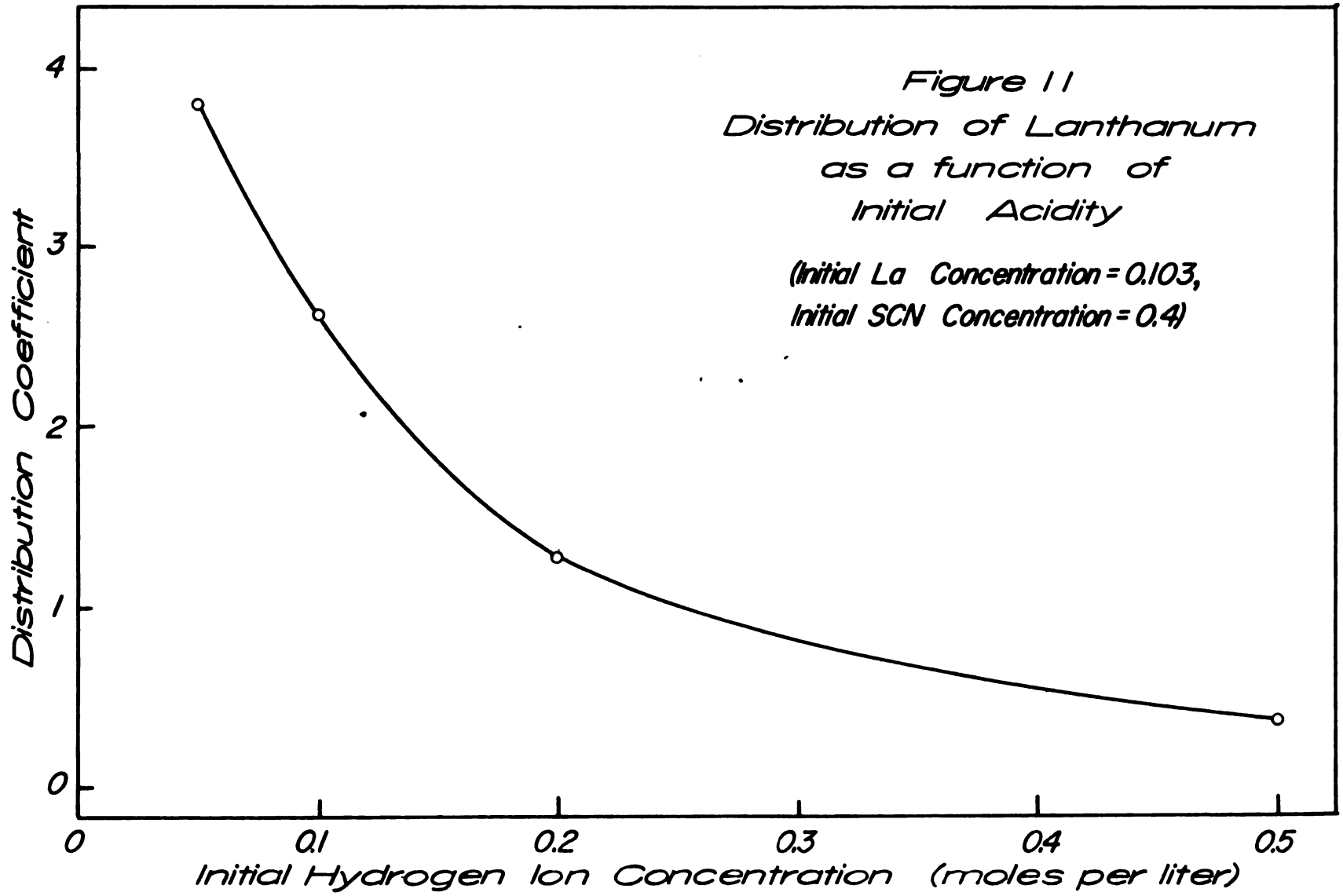

Figure 11
Distribution of Lanthanum
as a function of
Initial Acidity

(Initial La Concentration = 0.103,
Initial SCN Concentration = 0.4)

Table XIII

Extraction data for SCN from $La(SCN)_3$

Run No.	Concentration in Moles per Liter				Organic
	La Original	Acidity Original	SCN Original	SCN Organic	SCN/La Ratio
46	0.103	0.101	0.400	0.221	2.97
47	0.103	0.101	0.500	0.268	3.14
49	0.139	0.101	0.400	0.239	2.75
51	0.103	0.050	0.400	0.202	2.48
53	0.103	0.202	0.400	0.253	4.39
54	0.103	0.504	0.400	0.306	11.4

If one compares the data, it will be noticed that the distribution coefficients are not the same for the solutions using sodium thiocyanate as they are for the solutions in which ammonium thiocyanate was used, the distribution coefficients being greater for the solutions containing the sodium salt. In an attempt to explain this difference, which is too large to be accounted for by hydrolysis effects, extractions were made in which either ammonium or sodium thiocyanate solutions with no rare earth content were equilibrated with tri-n-butyl phosphate and the distribution of thiocyanate measured. This was done by analyzing both the aqueous and the organic phases for thiocyanate as described previously. Solutions of each were prepared and adjusted to be 0.6 formal with respect to the thiocyanate, and 0.1 formal with respect to perchloric acid. Upon analysis, it was found that the organic phase was 0.201 formal from the ammonium thiocyanate extraction, and only 0.125 formal from the sodium thiocyanate extraction. It appears from these data, that the

ammonium thiocyanate represses the extraction of the rare earths by being extracted itself. In order to determine whether sodium thiocyanate was being extracted, or if thiocyanic acid was the main species being extracted, a series of extractions were made in which the thiocyanate concentration was varied while the hydrogen ion concentration was held constant, and also in which the hydrogen ion concentration was varied as the thiocyanate concentration was held constant. The data for these extractions are given as Table XIV, and presented graphically as Figures 12 and 13.

Table XIV

Extraction data for NaSCN

Run No.	Concentration in Moles per Liter SCN Original	Acidity Original	SCN Organic
1	0.400	0.050	0.063
2	0.400	0.101	0.104
3	0.400	0.202	0.175
4	0.400	0.504	0.298
5	0.200	0.101	0.083
6	0.600	0.101	0.125

These data show that the concentration of thiocyanate in the organic phase increases rather markedly as the acidity is increased, but that there is only a slight increase in the amount of thiocyanate in the organic phase as the original thiocyanate concentration is increased. These observations indicate that the majority of the thiocyanate which enters the organic phase does so in the form of thiocyanic acid, and not as sodium thiocyanate.

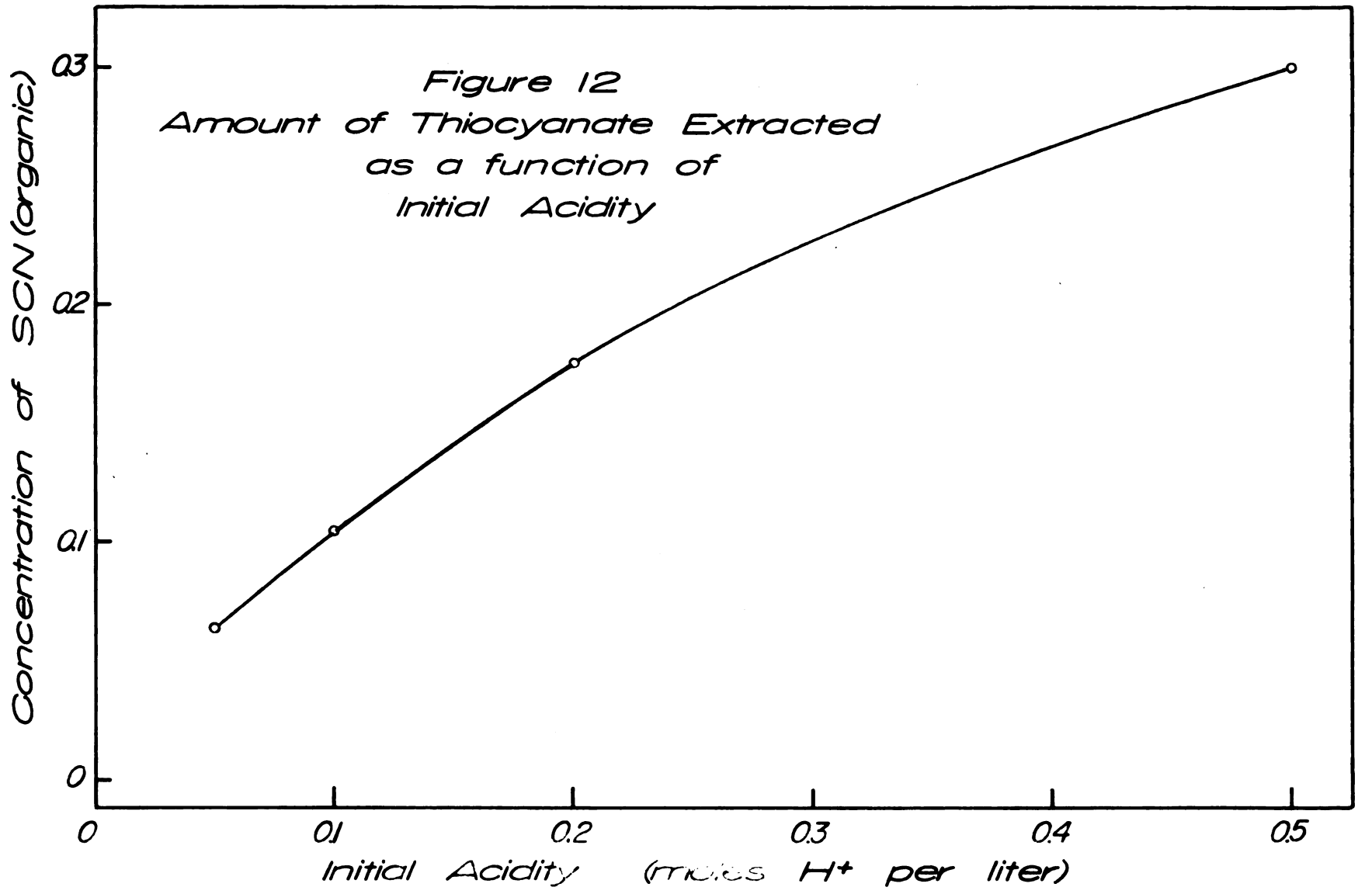
Figure 12
Amount of Thiocyanate Extracted
as a function of
Initial Acidity
Concentration of SCN (organic)
0.3
0.2
0.1
0
0
0.1
0.2
0.3
0.4
0.5
Initial Acidity (moles H+ per liter)

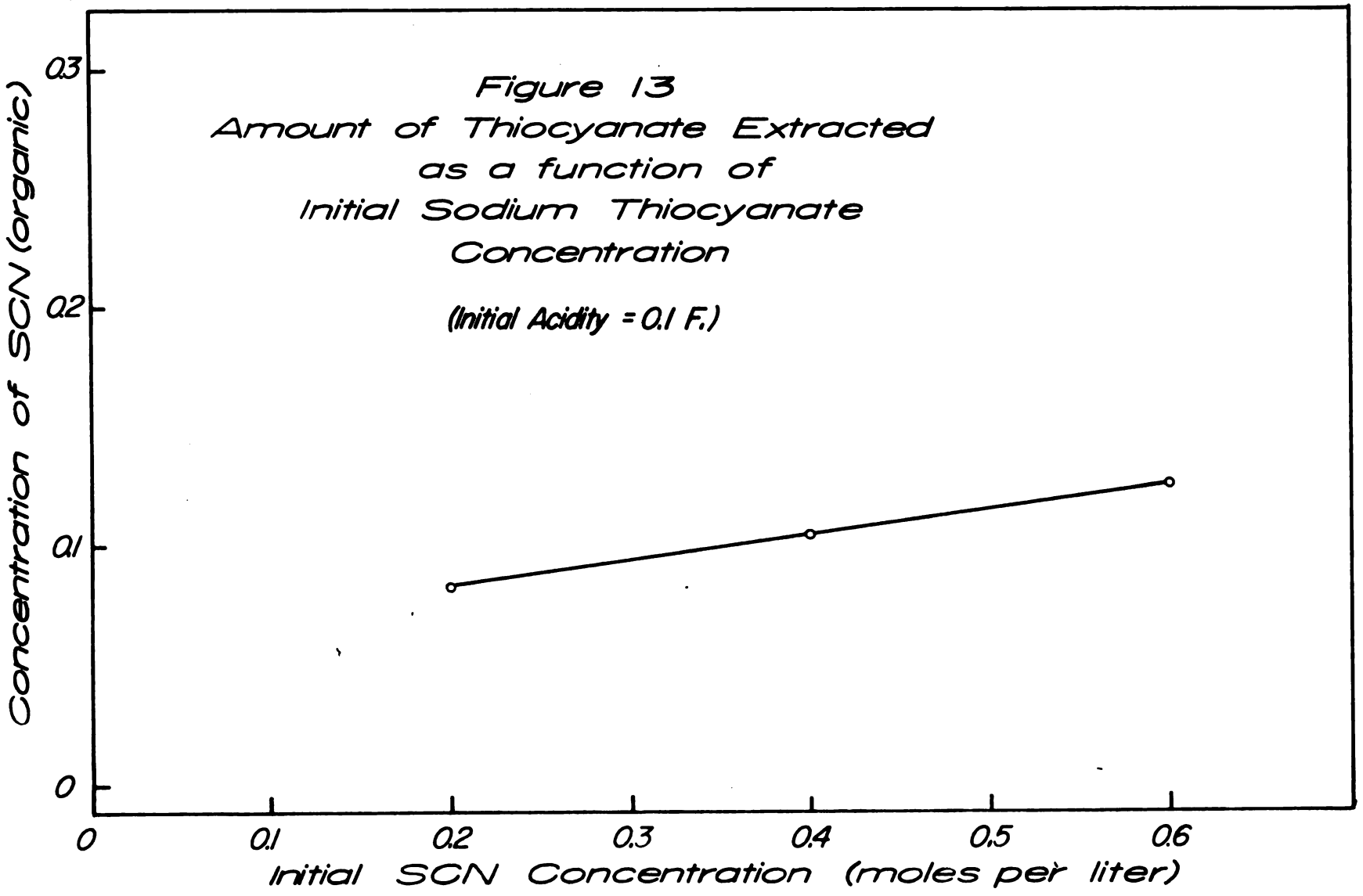
Figure 13
Amount of Thiocyanate Extracted
as a function of
Initial Sodium Thiocyanate
Concentration
(Initial Acidity = 0.1 F.)
Concentration of SCN (organic)
0.3
0.2
0.1
0
0
0.1
0.2
0.3
0.4
0.5
0.6
Initial SCN Concentration (moles per liter)

Extraction of Praseodymium Thiocyanate

The extraction of praseodymium was studied at different thiocyanate concentrations and at different initial acidities. Sodium thiocyanate was used to adjust the thiocyanate concentrations to the desired values, and perchloric acid was used to adjust the initial acidity. The ionic strength was adjusted by adding standard sodium perchlorate solution. The extractions were performed as described previously. The data obtained for these extractions are presented as Table XV, and graphically as Figures 14 and 15.

Table XV

Extraction data for Praseodymium

Run No.	Concentration in Moles per Liter					q
	Pr Original	Adidity Original	SCN Original	Pr Aqueous	Pr Organic	
1	0.103	0.101	0.000	0.0678	0.0349	0.515
2	0.103	0.101	0.200	0.0379	0.0648	1.71
3	0.103	0.101	0.400	0.0206	0.0821	3.99
4	0.103	0.101	0.600	0.0084	0.0943	11.23
5	0.103	0.050	0.400	0.0130	0.0897	6.90
6	0.103	0.202	0.400	0.0336	0.0691	2.06
7	0.103	0.504	0.400	0.0706	0.0321	0.455

These data show the same dependence on initial thiocyanate concentration and initial acidity as was observed for neodymium and lanthanum.

Extraction of Samarium Thiocyanate

The extraction of samarium was studied in exactly the same

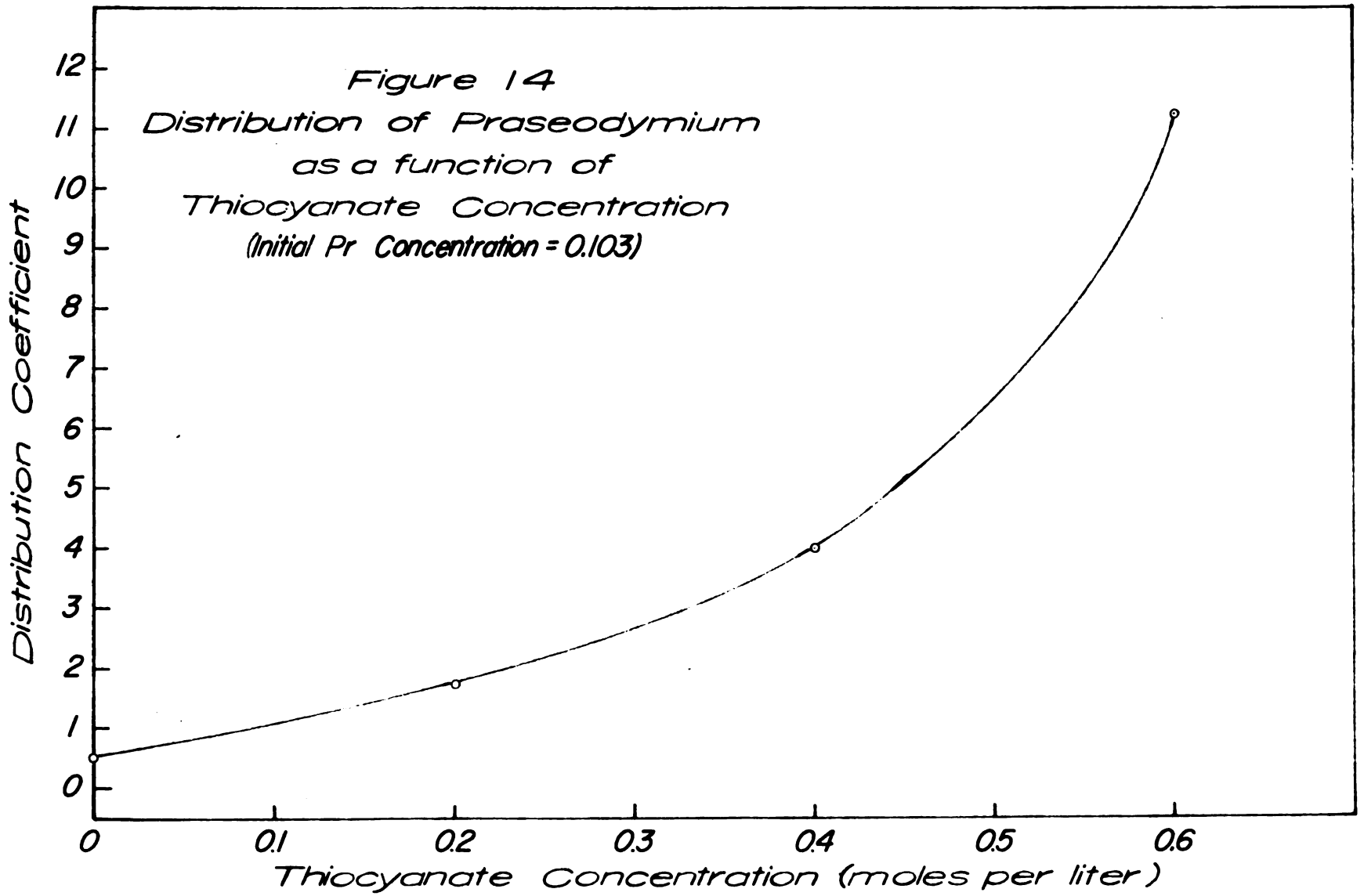
Figure 14
Distribution of Praseodymium
as a function of
Thiocyanate Concentration
(Initial Pr Concentration = 0.103)
Distribution Coefficient
0
1
2
3
4
5
6
7
8
9
10
11
12
0
0.1
0.2
0.3
0.4
0.5
0.6
Thiocyanate Concentration (moles per liter)

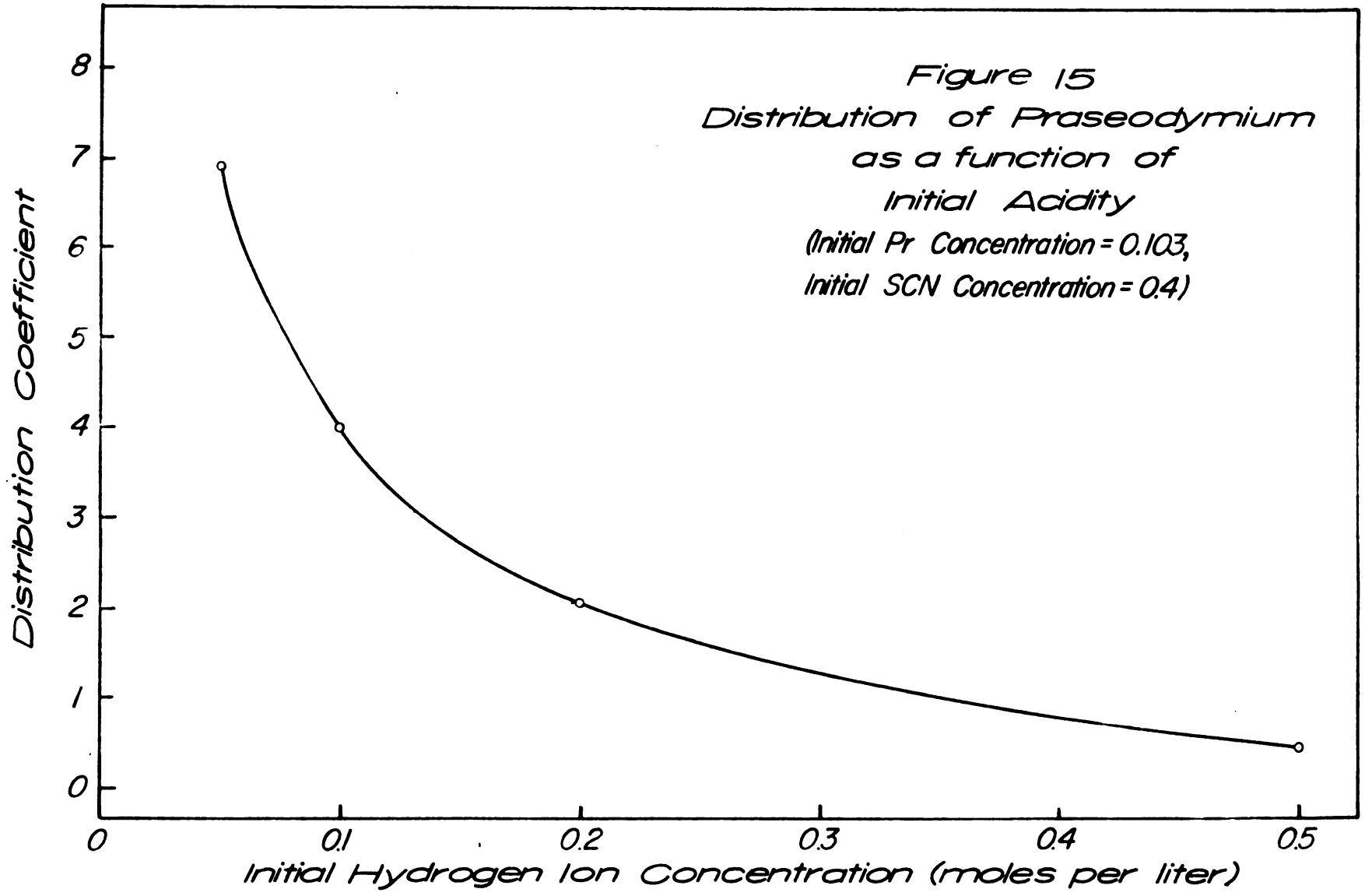

Figure 15
Distribution of Praseodymium
as a function of
Initial Acidity
(Initial Pr Concentration = 0.103,
Initial SCN Concentration = 0.4)

manner as was the praseodymium. The solutions to be extracted were made to be identical to those used in the praseodymium extraction, except that samarium was used instead of praseodymium. The results of these extractions are presented as Table XVI, and graphical representations of the data are given as Figures 16 and 17.

Table XVI

Extraction Data for Samarium

Run No.	Concentration in Moles per Liter					q
	Sm Original	Acidity Original	SCN Original	Sm Aqueous	Sm Organic	
1	0.103	0.101	0.000	0.0653	0.0374	0.573
2	0.103	0.101	0.200	0.0362	0.0665	0.84
3	0.103	0.101	0.400	0.0181	0.0846	4.67
4	0.103	0.101	0.600	0.0083	0.0944	11.37
5	0.103	0.050	0.400	0.0118	0.0909	7.70
6	0.103	0.202	0.400	0.0325	0.0702	2.16
7	0.103	0.504	0.400	0.0680	0.0347	0.510

These data show the same tendencies as were observed for the other rare earths studied.

Extraction of Praseodymium and Neodymium in the Presence of One Another

In order to test the usefulness of the extraction of the rare earth thiocyanates into tri-n-butyl phosphate, synthetic mixtures of praseodymium and neodymium thiocyanates were made, and these were equilibrated with tri-n-butyl phosphate as described before. Separation factors were determined spectrophotometrically by the method of Moeller and Brantley (40). The separation factor as used

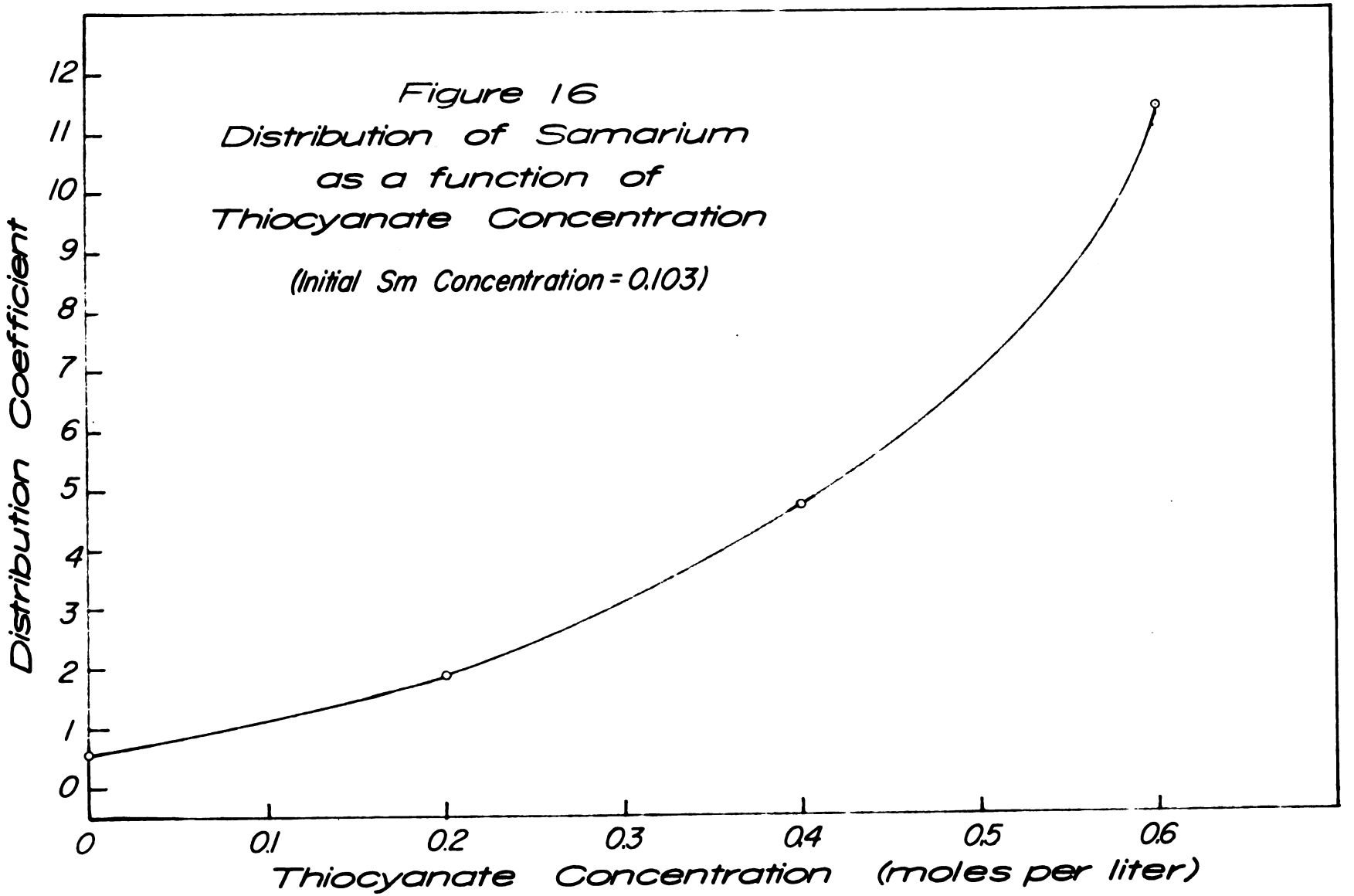
Figure 16
Distribution of Samarium
as a function of
Thiocyanate Concentration
(Initial Sm Concentration = 0.103)
Distribution Coefficient
0
1
2
3
4
5
6
7
8
9
10
11
12
0
0.1
0.2
0.3
0.4
0.5
0.6
Thiocyanate Concentration (moles per liter)

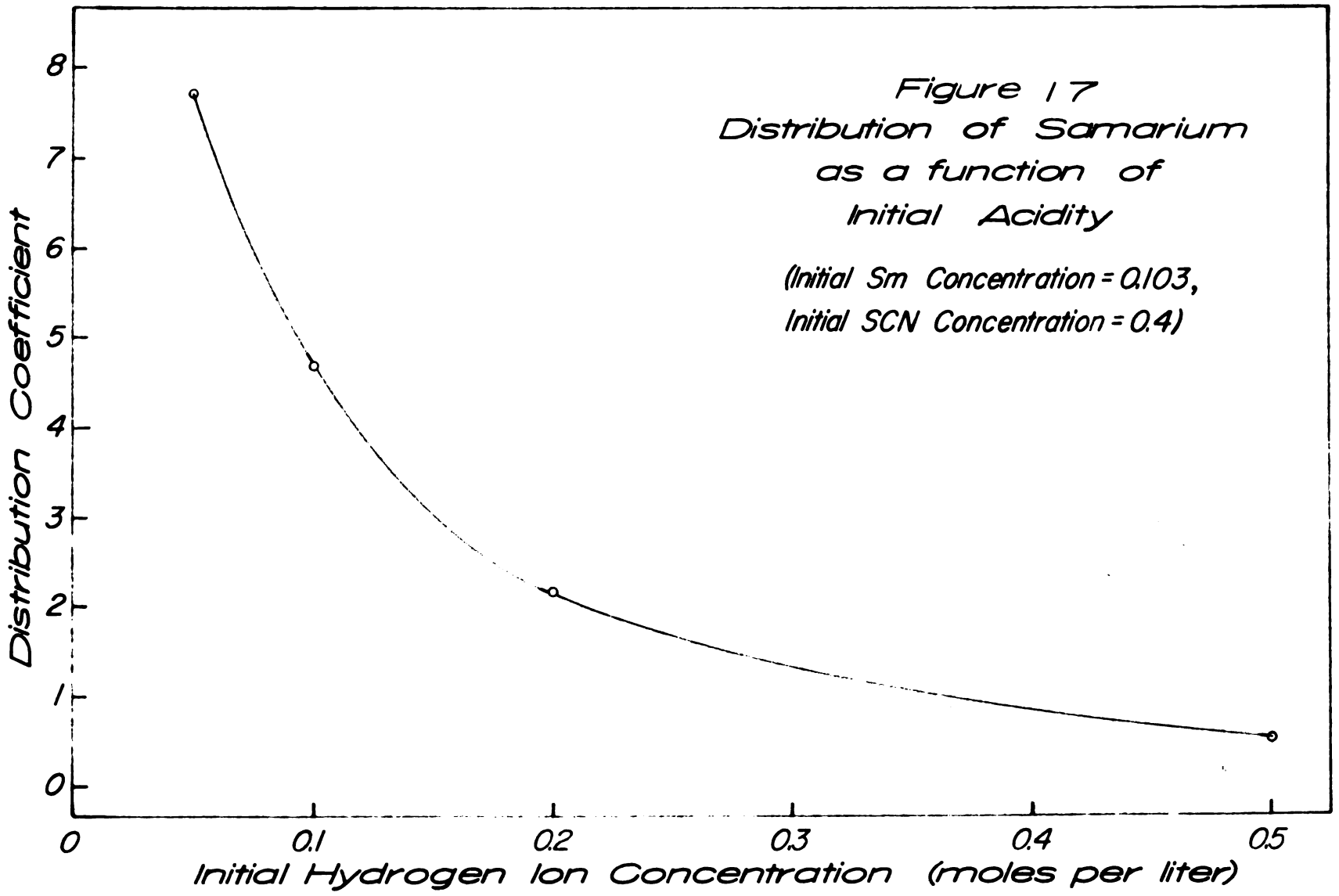

Figure 17
Distribution of Samarium
as a function of
Initial Acidity

(Initial Sm Concentration = 0.103,
Initial SCN Concentration = 0.4)

here is defined as the ratio of neodymium to praseodymium in the aqueous phase after extraction divided by the same ratio for the solution before extraction. The data from these experiments are listed as Table XVII.

Table XVII

Extraction of Neodymium and Praseodymium

Concentration in Moles per Liter				Separation
Nd Original	Pr Original	SCN Original	Acidity Original	Factor
0.075	0.025	0.400	0.101	1.14
0.050	0.050	0.400	0.101	0.95
0.025	0.075	0.400	0.101	0.77

These data indicate a variation of the separation factor as the relative amounts of different rare earths in a mixture were changed, even though the over-all concentration of rare earths were kept constant. It would appear, then, that this method would be of doubtful value for the separation of a crude mixture.

Cerium in the Presence of Thiocyanate

Since the distribution coefficients for lanthanum, praseodymium, neodymium, and samarium have been determined, it would be interesting to know the distribution behavior of cerous thiocyanate. A solution of cerous sulfate was prepared by reducing ceric sulfate with hydrogen peroxide, and sodium thiocyanate solution was added. Immediately upon the addition of thiocyanate, a voluminous precipitate of sulfur formed. To be certain that the

hydrogen peroxide was not the cause of the decomposition of the thiocyanate, sodium thiocyanate solution was added to an acidified solution of hydrogen peroxide, and the solution remained perfectly clear. The experiment with cerium was repeated with a fairly large excess of peroxide present to minimize the possibility of ceric cerium being present. When thiocyanate was added to this solution, the voluminous precipitate of sulfur was again very much in evidence. It was concluded that the difficulties in using cerium and thiocyanate together were too great to attempt a study of the cerium extraction.

Variations in the Absorption Spectra of the Rare Earths in Tri-n-butyl Phosphate Solutions

In the initial tests for the extractability of neodymium, both the aqueous and the organic phases were observed with a hand spectroscope, and it was noticed that the absorption bands seemed to have been shifted. It was decided that the visible spectra for the organic phase should be recorded and studied more carefully. Samples of the organic phase were taken, and their spectrum recorded using a Beckman model D.K.-2 recording spectrophotometer. From these spectra, it was noticed that the broad band which is observed at 574 millimicrons in aqueous solution had been partially resolved, and that the bands at 740 and 800 millimicrons had been shifted to longer wavelengths. The spectrum of neodymium perchlorate was not altered to the same extent as was the spectrum of the thio-

cyanate. In an attempt to explain these spectral shifts, some of the tri-n-butyl phosphate solution of the perchlorate was placed in an oven at 110° C. to remove most of the water dissolved in the solvent. The spectrum of this dried solution was completely different from that of the wet solution, and resembled more closely the spectrum of the thiocyanate solution. To see if the spectral changes were peculiar to tri-n-butyl phosphate, neodymium thiocyanate crystals were dissolved in methanol, and the spectrum of this solution recorded. This spectrum was almost identical to that of the thiocyanate in the tri-n-butyl phosphate. It appears that the shift in spectral bands in this case is merely a measure of the amount of water which is removed from the neodymium. Complete spectra of neodymium perchlorate in tri-n-butyl phosphate (not dried), neodymium thiocyanate in tri-n-butyl phosphate (not dried), and neodymium perchlorate in tri-n-butyl phosphate (dried) are presented as Figures 18, 19, and 20 respectively. Detailed spectra of only the region 560 - 620 millimicrons of neodymium perchlorate in water solution, neodymium thiocyanate in methanol, and the solutions described above are presented as Figures 21 through 25.

Spectra were recorded for praseodymium and samarium thiocyanate in tri-n-butyl phosphate, but these do not show any appreciable difference from that in the aqueous phase. These spectra are presented as Figures 26 and 27.

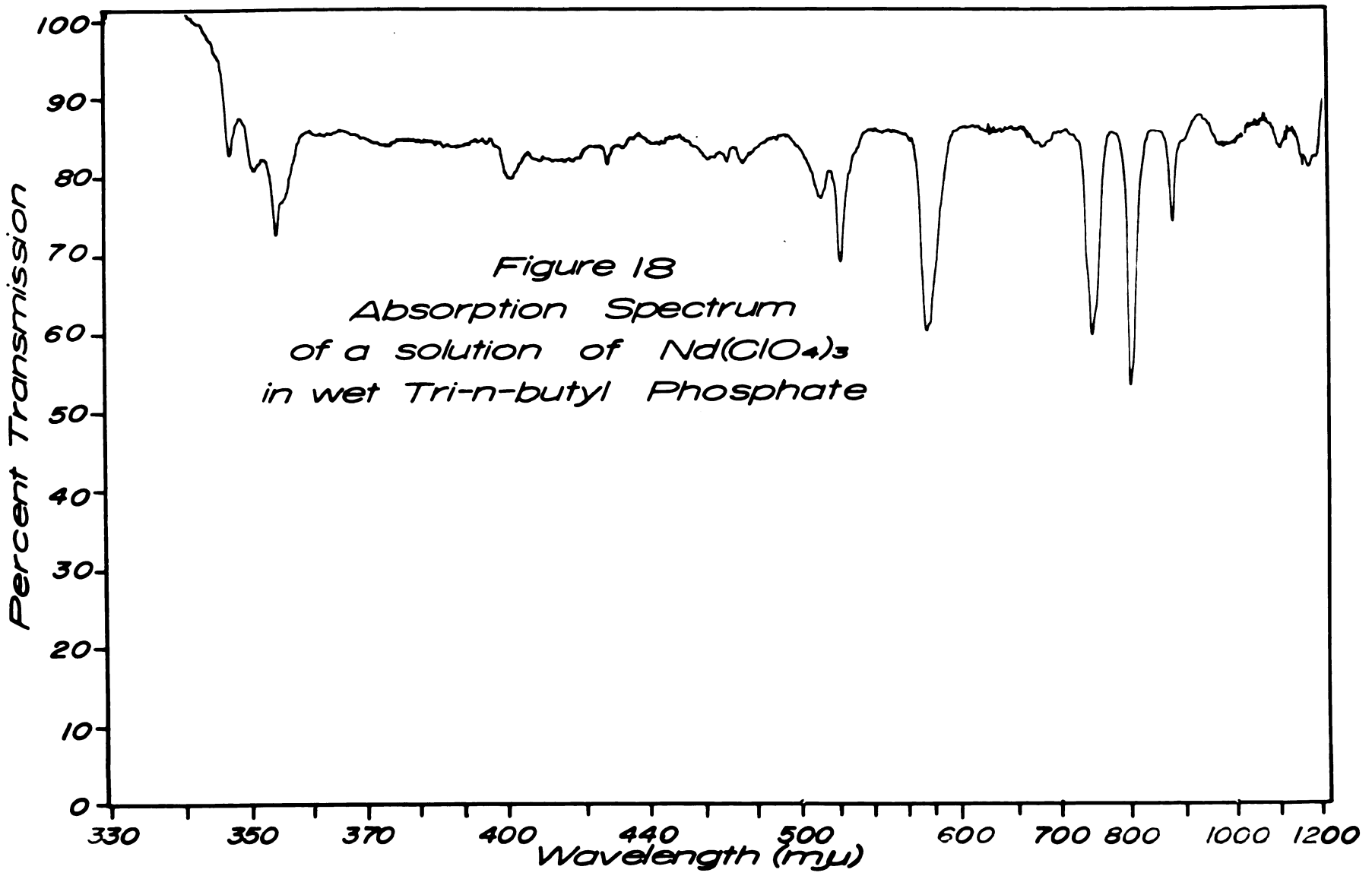

Figure 18
Absorption Spectrum
of a solution of $Nd(ClO_4)_3$
in wet Tri-n-butyl Phosphate

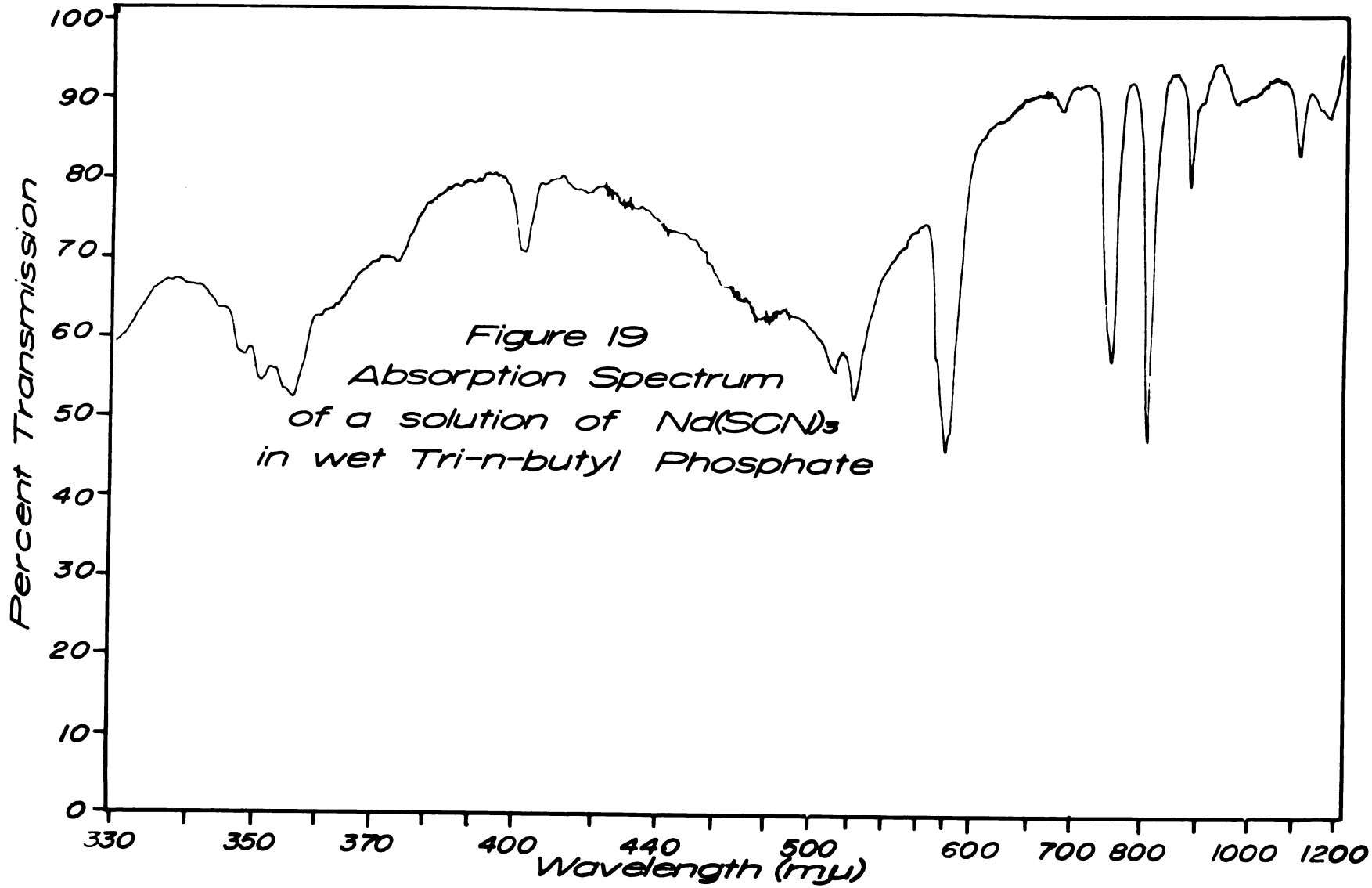

Figure 19
Absorption Spectrum
of a solution of $Nd(SCN)_3$
in wet Tri-n-butyl Phosphate

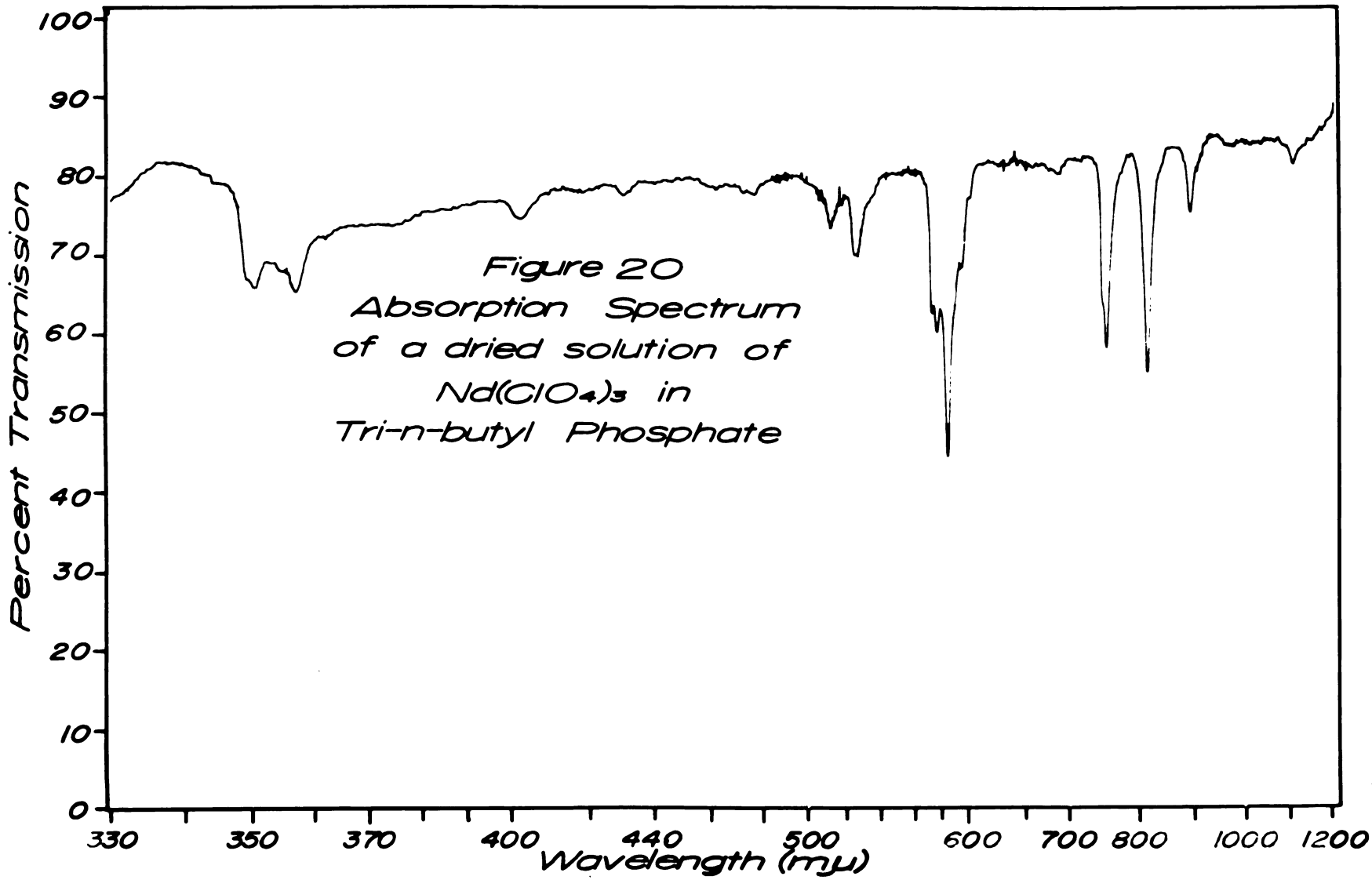

Figure 20
Absorption Spectrum
of a dried solution of
$Nd(ClO_4)_3$ in
Tri-n-butyl Phosphate

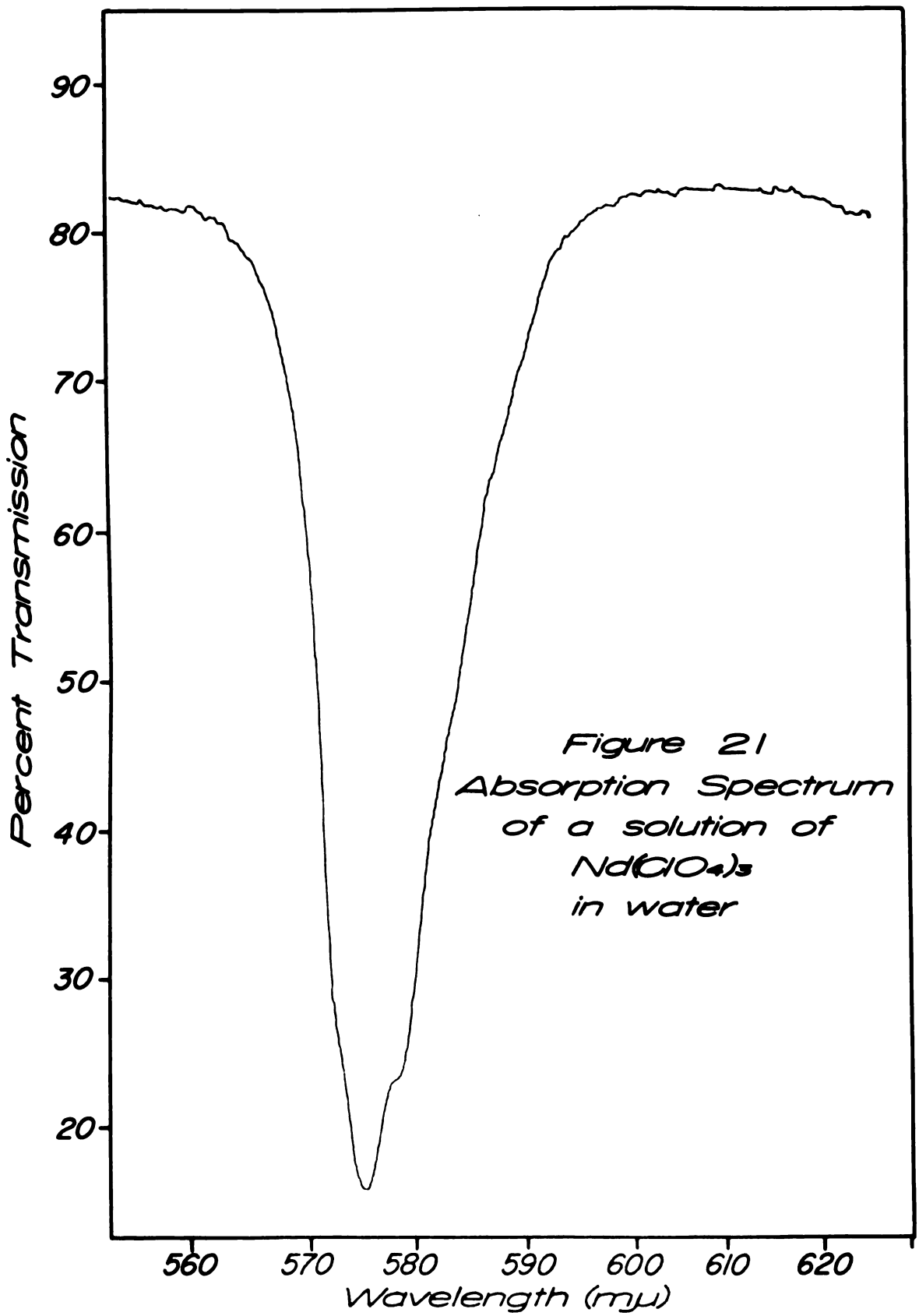

Figure 21
Absorption Spectrum
of a solution of
$Nd(ClO_4)_3$
in water

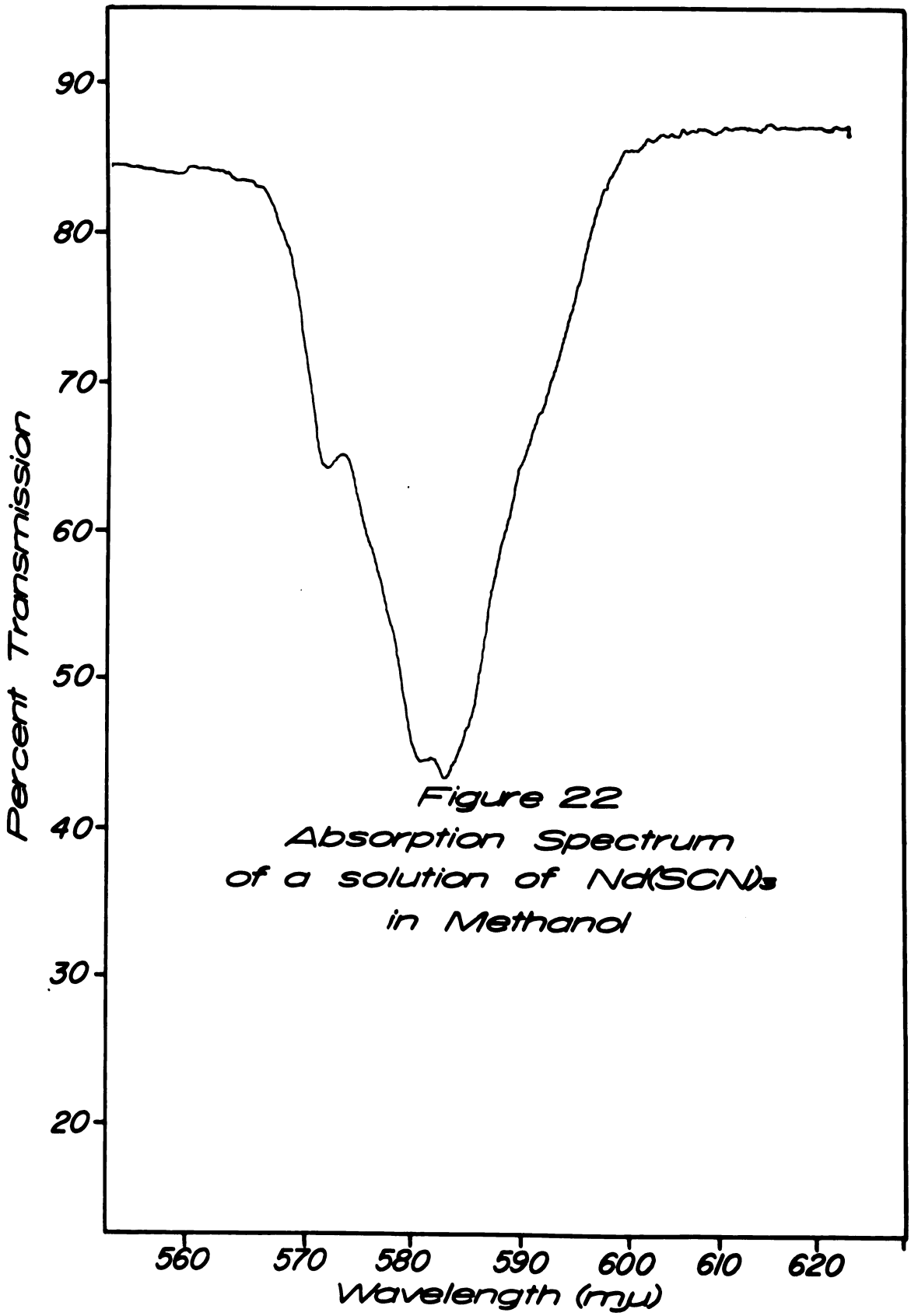

Figure 22
Absorption Spectrum
of a solution of $Nd(SCN)_3$
in Methanol

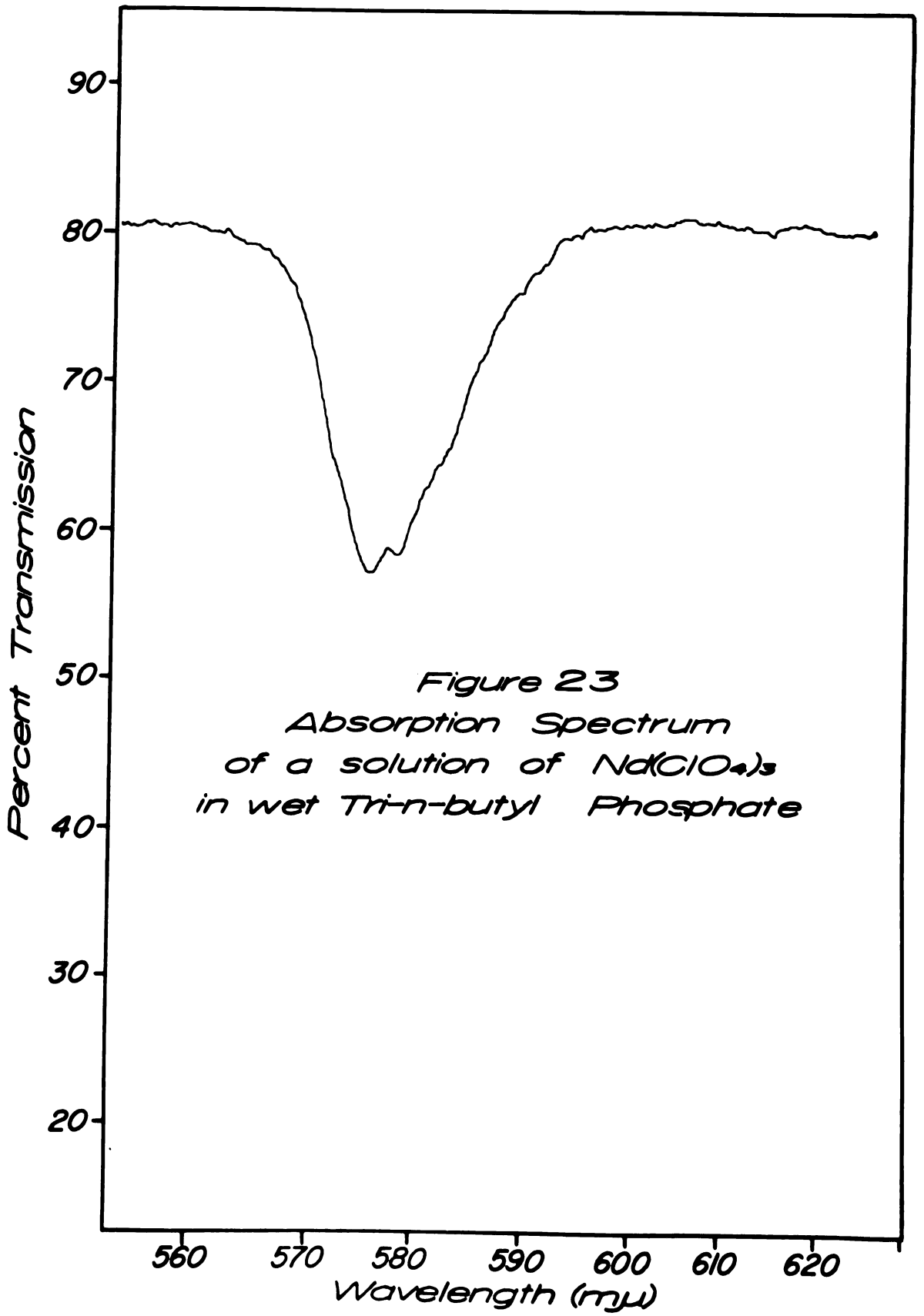

Figure 23
Absorption Spectrum
of a solution of $Nd(ClO_4)_3$
in wet Tri-n-butyl Phosphate

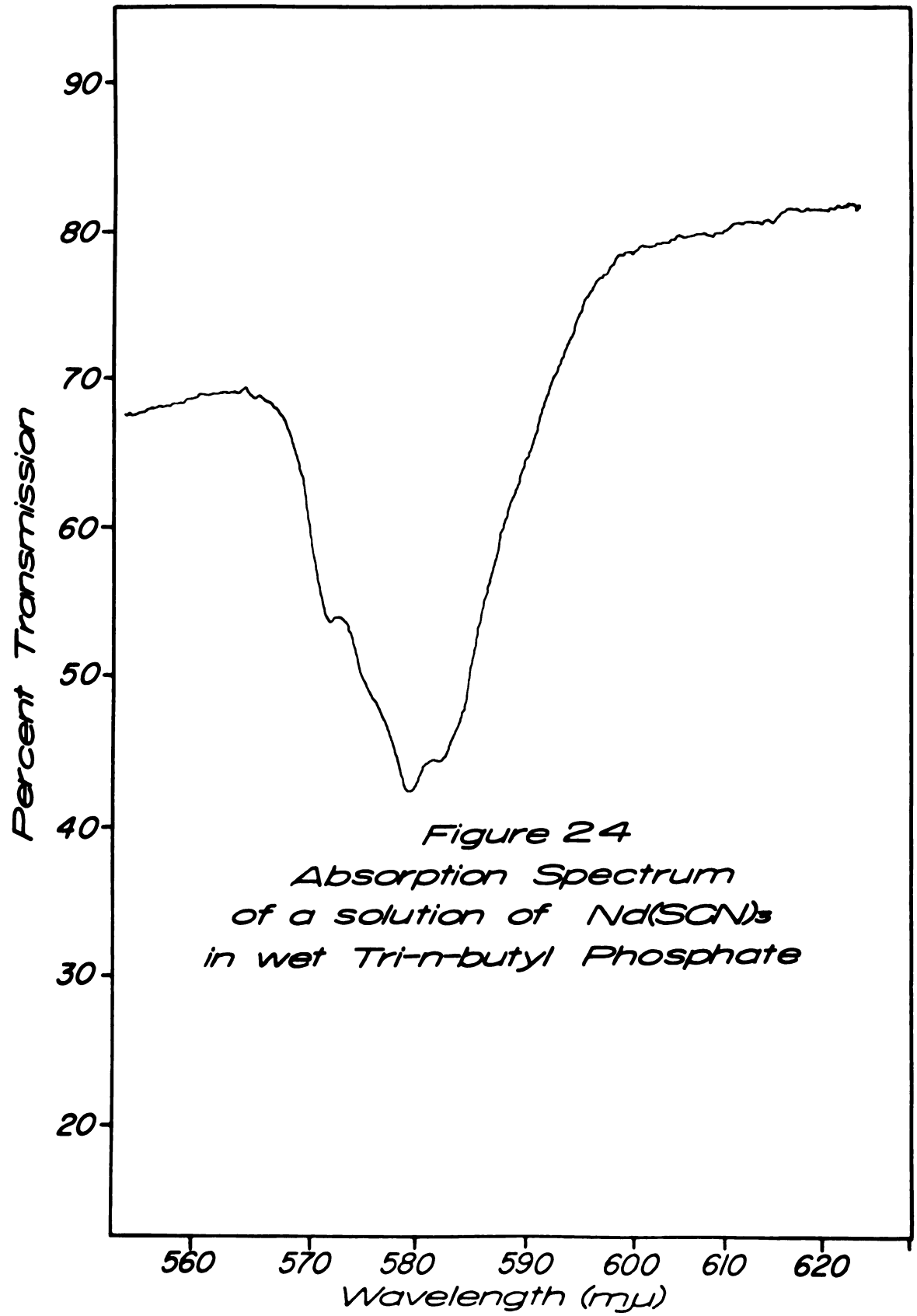

Figure 24
Absorption Spectrum
of a solution of $Nd(SCN)_3$
in wet Tri-n-butyl Phosphate

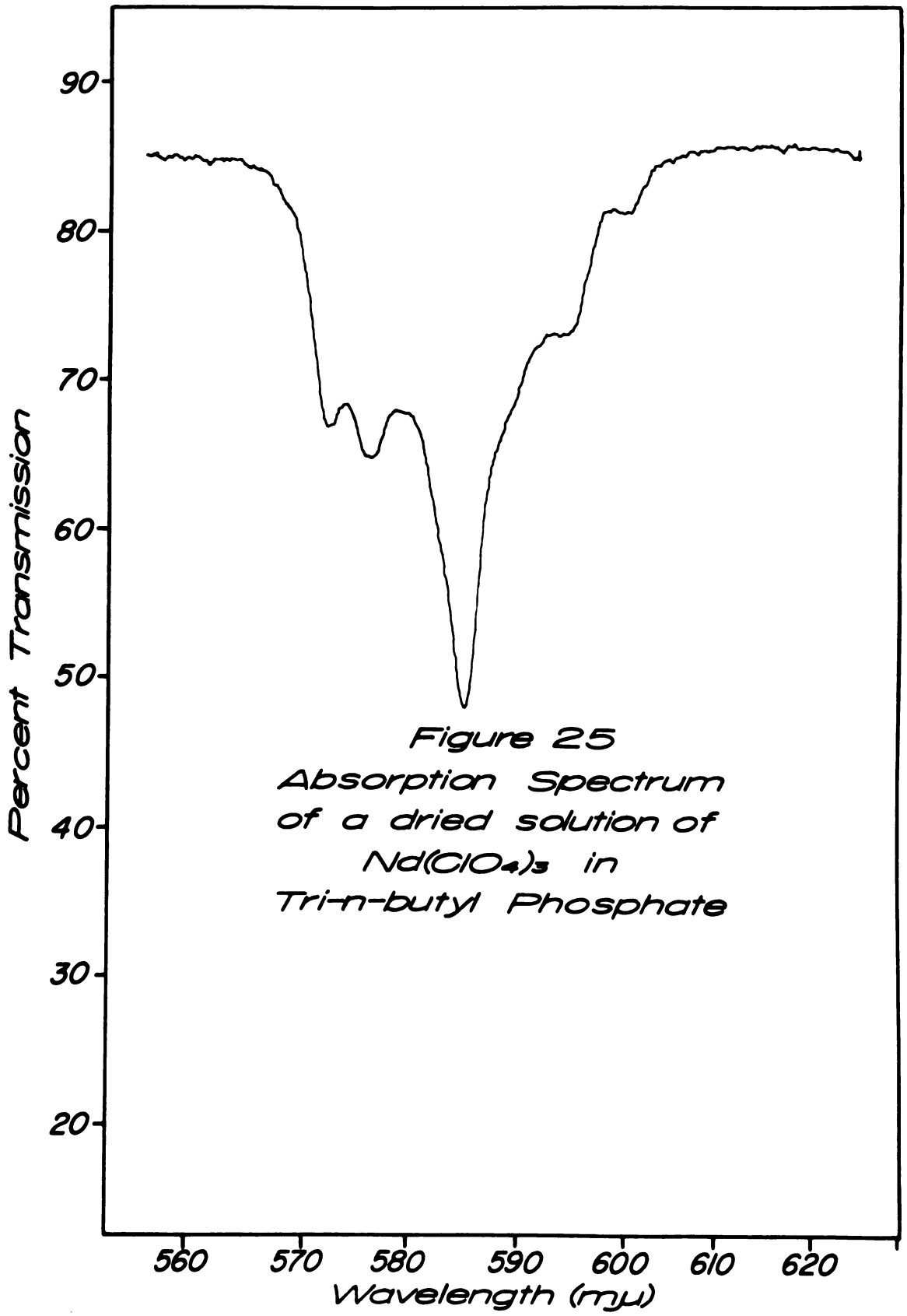

Figure 25
Absorption Spectrum
of a dried solution of
$Nd(ClO_4)_3$ in
Tri-n-butyl Phosphate

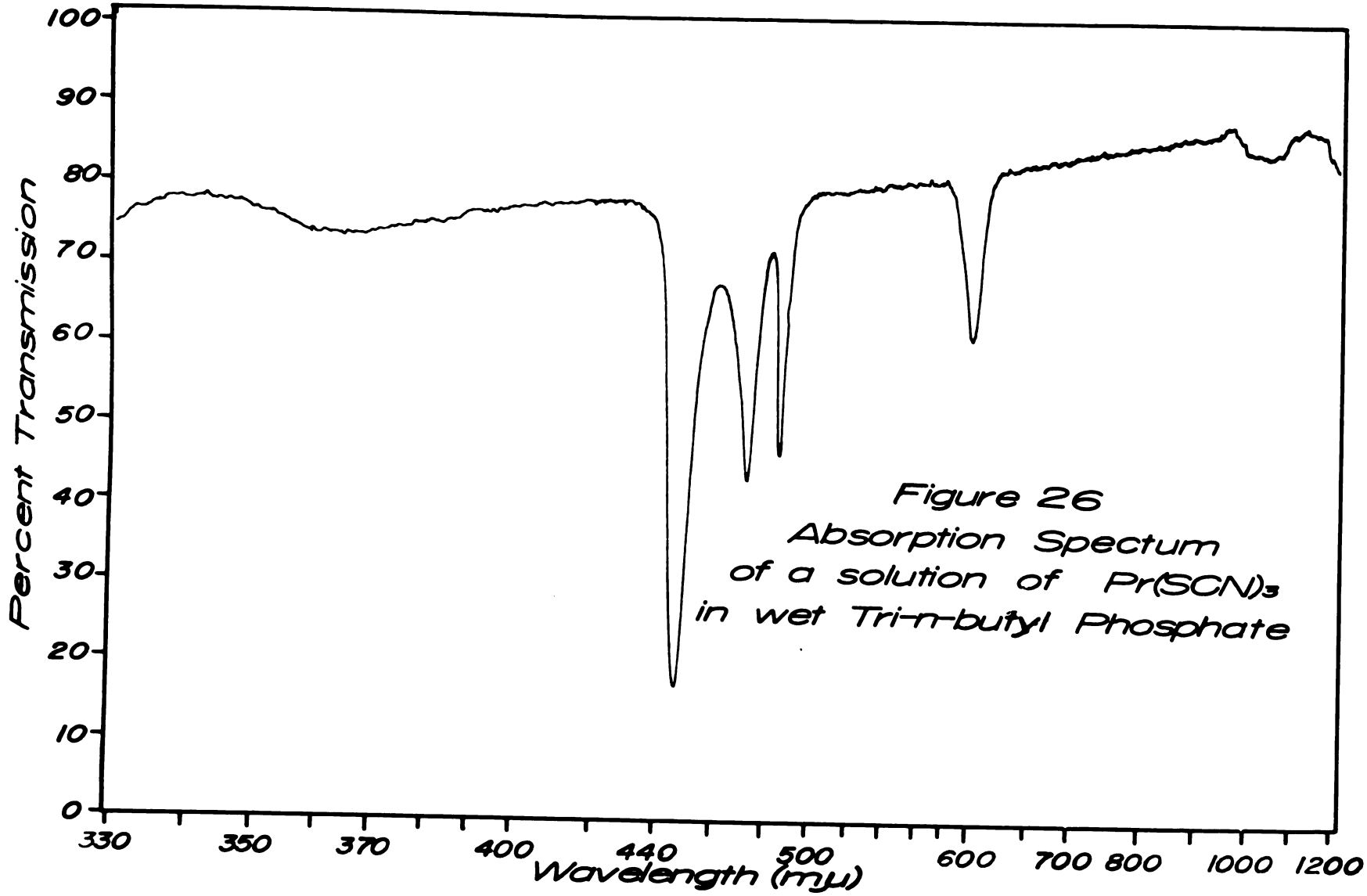

Figure 26
Absorption Spectum
of a solution of $Pr(SCN)_3$
in wet Tri-n-butyl Phosphate

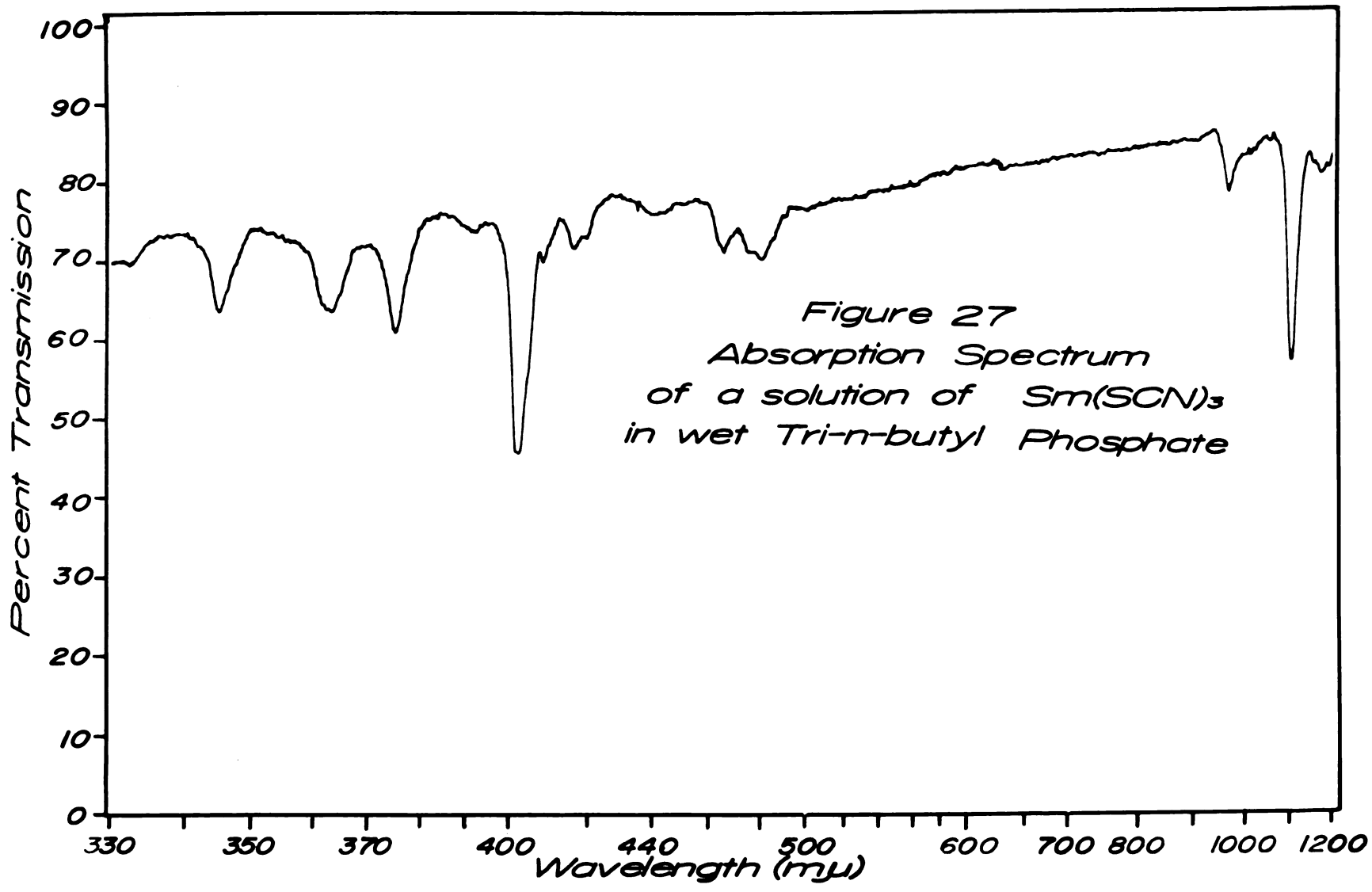

Figure 27
Absorption Spectrum
of a solution of $Sm(SCN)_3$
in wet Tri-n-butyl Phosphate

The Effect of a Small Amount of Iron on the Distribution of Neodymium Thiocyanate

The color of the neodymium thiocyanate in the tri-n-butyl phosphate was redder than are neodymium solutions in general, and the absorption spectrum of these solutions showed a general absorption in the region of 440 to 550 millimicrons. This is the region of absorption of the ferric thiocyanate complex. In order to determine whether the amount of iron which would produce this amount of absorption would have any effect on the distribution of neodymium, an extraction was made in which the neodymium was all added as the perchlorate, and the thiocyanate was all added as sodium thiocyanate. In this extraction, the tri-n-butyl phosphate phase had the usual color of neodymium salts, and the change in distribution coefficient was approximately that which was observed in the lanthanum salts for a change in ionic strength equal to the change in ionic strength between the neodymium solutions being compared. To make certain that this was the only cause for the difference, the extraction was repeated with enough ferric chloride solution added to make the solution 0.0001 formal with respect to iron. The color of the tri-n-butyl phosphate phase from this extraction was such an intense red that the solution was almost opaque. The distribution coefficient of neodymium was completely unchanged, however. It can be said, then, that small amounts of iron as an impurity would have no effect on the distribution of neodymium.

The Extraction of Lanthanum Thiocyanate at 35° C.

In order to check the magnitude of the effect of changing temperature on the extraction of lanthanum thiocyanate, one extraction was made at 35° C. For this experiment, the same solution was used as in run number 52. The distribution coefficient was found to be 2.98, which is to be compared with 2.71 for run number 52, at 25° C. This indicates that the extraction is enhanced by the higher temperature, but not by a significant amount. Since the distribution coefficient amplifies any difference in two solutions, it is perhaps better to compare the concentration of the lanthanum in the organic phase for the two solutions. At twenty-five degrees, the concentration of lanthanum in the organic phase was 0.0750, and at thirty-five degrees, the concentration was 0.0769. This is a difference of only 2.5 percent.

DISCUSSION

Previous work on the distribution of rare earths between water and non-aqueous solvents has all been qualitative in nature, in that no attempt was made to elucidate the species crossing the phase boundary, or the species present in either phase. There is a large number of possible species present in each of the phases, this number being considerably reduced for those which may cross the phase boundary, because only uncharged species can be transported from one phase to another. Some of the species which might be present in the thiocyanate system are $M(SCN)_3$, $M(SCN)_2^+$, $M(SCN)^{++}$, M^{+++}, SCN^-, HSCN, $HM(SCN)_4$, $M(SCN)_4^-$, $H_2M(SCN)_5$, etc. As pointed out at the beginning of the experimental section, the experiments described in this thesis were designed to shed some light on which of these species were important in the distribution of the rare earth thiocyanates between water and tri-n-butyl phosphate. In the interpretations which follow, much must remain somewhat qualitative, in that some of the important variables of the system cannot be measured. For instance, the "free" metal ion concentration, as such, cannot be measured in either phase; only the total metal concentration in each phase can be determined analytically. The "free" thiocyanate ion concentration cannot be measured easily, although a potentiometric method utilizing a silver-silver thiocyanate electrode system would probably give a fair value for this quantity. In this study, however, the total

thiocyanate in each phase was estimated by precipitation of the thiocyanate with silver nitrate solution. With these limitations in mind, and with the method of Irving et al. (31) described in the theoretical section serving as a guide, the results described in the experimental section can now be discussed.

Effect of Thiocyanate Ion Concentration on the Distribution Coefficient of the Rare Earths

If the mechanism of the extraction of the rare earth thiocyanates involves some type of complex between the rare earth ion and the thiocyanate ion (such as $M(SCN)_3$, $M(SCN)_4$, etc.), changing the concentration of thiocyanate in the aqueous phase should have a pronounced effect on the extraction coefficient. For the discussion of this effect, lanthanum will be presented as a typical example.

The addition of thiocyanate ion to the aqueous solution before extraction has a pronounced effect on the amount of lanthanum which enters the organic phase. The data (Tables IX, XI, and XII) presented graphically in the experimental section (Figures 7 through 10) indicate an increase in the amount of lanthanum extracted as the original thiocyanate ion concentration is increased, while the concentration of lanthanum was held constant. In order to treat this extraction according to the method of Irving et al., the "free" thiocyanate ion concentration after extraction is needed. If the "free" thiocyanate ion concentration is assumed

to be equal to or proportional to the total thiocyanate concentration after extraction, then the variation of the distribution coefficient with thiocyanate may be analyzed by utilizing equation (5) from the theoretical section:

$$\log q = A + \log(\bar{m}_o/\bar{m}) + (\bar{m}_o\bar{h}_o - \bar{m}\bar{h})\log(H) + (\bar{n}_o - \bar{n})\log(M) + (\bar{n}_o\bar{n}_o - \bar{m}\bar{n})\log(N).$$

If the thiocyanate ion concentration is the only variable, then the slope of a plot of log q (the distribution coefficient) versus log(SCN^-) would represent the value ($\bar{m}_o\bar{n}_o - \bar{m}\bar{n}$), the difference between the average number of thiocyanate ions associated with the complex in the organic phase ($\bar{n}_o\bar{n}_o$)and the average number associated with the complex in the aqueous phase ($\bar{m}\bar{n}$). (Note that these are average values, and do not necessarily represent the most important species present.) A logarithmic plot of this type is presented as Figure 28. From the slopes of the lines in this figure, the value of the quantity ($\bar{n}_o\bar{n}_o - \bar{m}\bar{n}$) is found to be two, which means, for the average composition, there are two more thiocyanates associated with the lanthanum in the organic phase than there were with the lanthanum in the aqueous phase. Unless the number of thiocyanate ions associated with the lanthanum in one phase is known, however, nothing definite may be said about the average number associated with the lanthanum in the other phase. If the value of four for the average number of thiocyanates associated with each lanthanum, $\bar{n}_o$, which was indicated in one

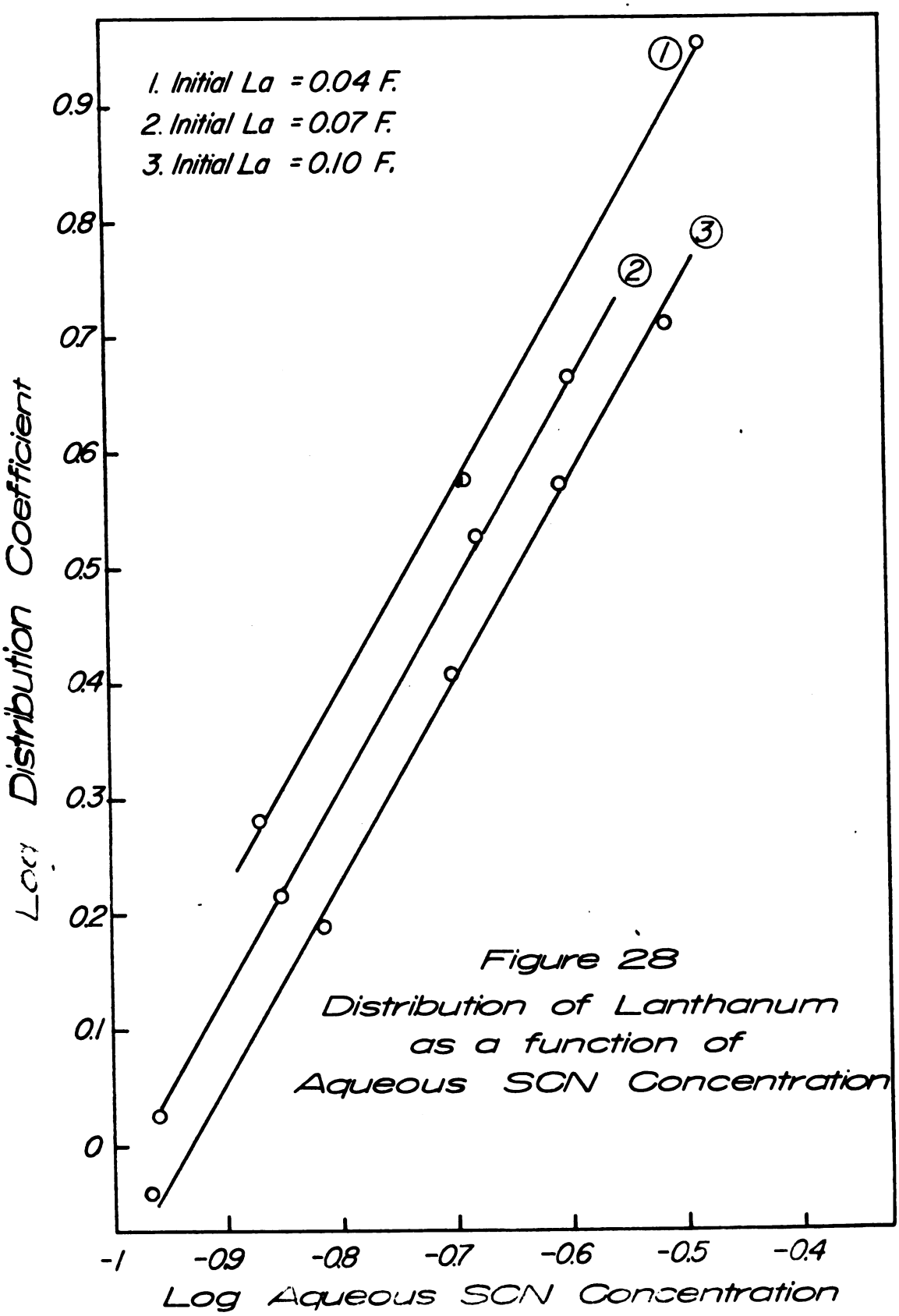

Figure 28
Distribution of Lanthanum
as a function of
Aqueous SCN Concentration

series of determinations (Table X) is assumed to be correct, then this treatment leads us to believe that the average composition in the aqueous phase is something of the nature of $La(SCN)_2^+$. Other determinations of thiocyanate to lanthanum ratios in the organic phase (Table XIII) tend to show that the ratio of four to one indicated above was due mostly to coincidence, and that the four to one ratio in the organic phase does not necessarily represent the average composition. From these other data, it appears that the lanthanum in the organic phase is present as anything from $La(SCN)_2^+$ to $La(SCN)_6^{---}$. Subtracting two thiocyanates from these average species in the organic phase to give the average composition of the aqueous would then imply that anything from La^{+++} to $La(SCN)_4^-$ could be the average composition of the lanthanum in the aqueous phase. This treatment gives no information relative to the actual species crossing the phase boundary, but only the average association after the lanthanum has entered the organic phase. The main conclusion which can be drawn is that there is some form of thiocyanate complex or ion aggregate present in each phase.

Since some of the thiocyanate to lanthanum ratios for the organic phase reported above are less than three, it must be implied that the perchlorate ion, used to control the ionic strength, is entering into the extraction. To learn the magnitude of the extraction of lanthanum perchlorate, an experiment was performed in which no thiocyanate was present. The distribution coefficient obtained for this experiment (Table XI. Run number L36) was

approximately 0.5. This comparatively high extraction coefficient for lanthanum perchlorate alone indicates the average composition of the species crossing the phase boundary may be anything from $La(ClO_4)_3$ to $HLa(SCN)_4$, depending upon the initial conditions. This extraction also indicates either that the perchlorates of the rare earths are more associated in the aqueous phase than has previously been assumed, that the distribution coefficient of the extracted species is exceptionally high, or that the lanthanum perchlorate is also almost completely dissociated in the tri-n-butyl phosphate. The distribution experiments performed using praseodymium, neodymium, and samarium show a similar dependence on the initial thiocyanate concentration, and therefore indicate similar conclusions.

Dependence of the Distribution of Rare Earth Thiocyanate on the Aqueous Rare Earth Concentration

In order to learn whether the distribution coefficient of the rare earths was a function of the rare earth concentration, a series of experiments were performed in which the rare earth concentration was varied while the acidity and the thiocyanate ion concentrations were kept constant. As in the previous discussion, lanthanum is cited as a typical case.

The fact that at equal initial thiocyanate ion concentrations the distribution of lanthanum decreases with increasing lanthanum concentration (retrograde extraction) is evident from the graphical presentation of the data (Figure 15). Again, in order to treat

this extraction according to the method of Irving et al, the "free" lanthanum ion concentration in the water phase after extraction is needed. If the assumption is made that the "free" lanthanum concentration is nearly equal to or proportional to the total aqueous lanthanum after extraction, equation (5) may again be utilized. If the lanthanum concentration is the only variable, then the slope of a plot of log q versus log (La) would represent the difference $(\bar{n}_o - \bar{n})$ in the average association of the lanthanum in the organic phase $(\bar{n}_o)$ and the average association in the aqueous phase $(\bar{n})$. Such a plot is presented as Figure 29. From this graph, the value of $(\bar{n}_o - \bar{n})$ is found to be -5/16, which would indicate that on the average there are one and five sixteenths lanthanum ions associated with one another in the aqueous phase. This value for the average association in the aqueous phase means that about 48 percent of the total lanthanum in the aqueous phase is present as a dimer. The existence of lanthanum thiocyanate in the aqueous phase as a dimer is a rather unlikely postulate, so another explanation was desired.

Brubaker (13) has recently studied the extraction of tellurium (IV) chloride into bis(2-chloroethyl)ether from aqueous hydrochloric acid solutions, and shows that the phenomenon of retrograde extraction may be explained in another manner. Transforming his equations so that they correspond to the case of lanthanum thiocyanate instead of tellurium tetrachloride, his reasoning, briefly stated, is as follows.

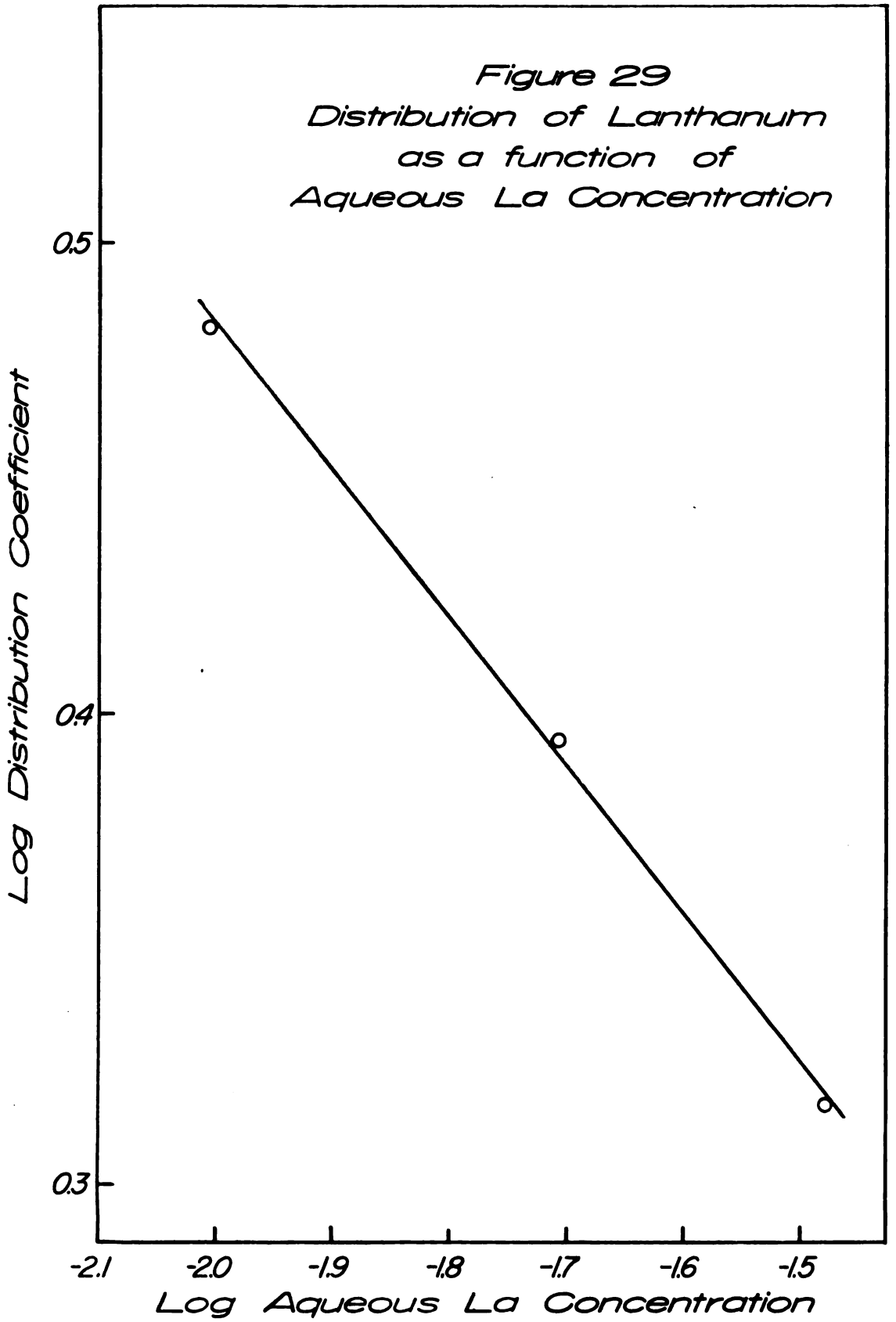
Figure 29
Distribution of Lanthanum
as a function of
Aqueous La Concentration
0.5
0.4
0.3
Log Distribution Coefficient
-2.1
-2.0
-1.9
-1.8
-1.7
-1.6
-1.5
Log Aqueous La Concentration

If the extracted species are lanthanum thiocyanate and tetrathiocyanatolanthanic acid, and the complex acid dissociates in the organic phase to form $La(SCN)_4^-$, the distribution coefficient, q, is

$$q = \frac{(La(SCN)_3)_o + (HLa(SCN)_4)_o + (La(SCN)_4^-)_o}{(La)_w} ,$$

where parentheses represent molar concentrations, and the subscripts o and w distinguish between the organic and the aqueous solutions respectively. This equation may be rewritten in the form

$$q = K_D\left\{1 + K_1(HSCN)_o + \frac{K_1K_2(HSCN)_o}{(H^+)_o}\right\} , \text{ where}$$

$$K_D = \frac{(La(SCN)_3)_o}{(La)_w} , \qquad K_1 = \frac{(HLa(SCN)_4)_o}{(HSCN)_o(La(SCN)_3)_o} ,$$

$$K_2 = \frac{(H^+)_o(SCN^-)_o}{(HSCN)_o} , \text{ and} \qquad K_3 = \frac{(H^+)_o(La(SCN)_4^-)_o}{(HLa(SCN)_4)_o} .$$

Using the above relationships, the concentration of the "free" hydrogen ion in the organic phase may be calculated by means of the following equation:

$$(H^+)_o = \left\{K_2(HSCN)_o + K_1K_3K_D(HSCN)_o(La)_w\right\}^{\frac{1}{2}} .$$

For the tellurium extraction, Brubaker was able to evaluate K_D from experimental results, and K_1 spectrophotometrically, and found that by properly choosing the values K_2 and K_3, he could fit the experimental data to those predicted by the

above equation quite well. It is possible that the extractions studied in this thesis could also be explained by a similar treatment, but the determination of the constant K_1 is not possible for this system because there does not appear to be any appreciable difference in the spectral properties of the two species.

Of the two mechanisms for explaining retrograde extraction of the lanthanum thiocyanate, (a) the existence of a dimer, and (b) the ionization and dissociation of the complex in the organic phase, it is felt that the explanation presented by Brubaker is the more plausible of the two explanations. The dependence of the distribution of neodymium thiocyanate on the initial concentration of neodymium indicate a similar conclusion in that the distribution coefficient decreases with increasing neodymium concentration.

Dependence of the Extraction of Rare Earth Thiocyanate On the Acidity of the Aqueous Phase

The effect of a variation of the initial acidity of the aqueous solution on the distribution of the metal is essentially the same for lanthanum, neodymium, praseodymium, and samarium. In the discussion which follows, lanthanum is used as being representative of the other rare earths.

Increasing the acidity of the lanthanum thiocyanate solution to be equilibrated with tri-n-butyl phosphate decreases the extraction of the lanthanum considerably, as can be seen from the

data (Table XII) presented graphically (Fig. 11) in the experimental section. If a complex acid such as $HLa(SCN)_4$ were the species crossing the phase boundary, it might be expected that since thiocyanic acid is a comparatively strong acid (60), the extraction of lanthanum would be enhanced by the addition of acid. The fact that the reverse of this is naturally the case does not necessarily prove that the extracted species is not a complex acid, however. If we recall the experimental results on the extraction of thiocyanate from a solution of sodium thiocyanate as a function of the original acidity (Table XIV, Figures 12 and 13) it will be remembered that thiocyanic acid appears to be the species extracted. If we combine these results with those of the lanthanum extraction, we may show that the extraction of a complex acid such as $HLa(SCN)_4$ will be decreased if another stronger acid is extracted simultaneously. The reasoning behind this argument is that if the species crossing the phase boundary is an acid of the type proposed above, then it is the concentration of this species in each phase which is the controlling factor in the extraction. If the complex acid can dissociate into ions such as H^+ and $La(SCN)_4^-$ in the organic phase, then this dissociation will reduce the concentration of the undissociated $HLa(SCN)_4$ in that phase. Likewise, if anything were present which would repress this dissociation, then the concentration of the undissociated acid would be increased. This repression of the dissociation of $HLa(SCN)_4$ in the organic phase is just what appears to happen when thiocyanic acid is introduced. The thiocyanic

acid is extracted into the organic phase and undoubtedly dissociates - (at least partially) - into hydrogen ions and thiocyanate ions. The increase in hydrogen ion concentration represses the ionization of the $HLa(SCN)_4$ which in turn prevents more lanthanum from crossing the phase boundary. This is only one explanation of the effect of the acidity on the extraction of lanthanum, namely the assumption of an acid complex as the important species crossing the phase boundary.

The effect of acidity may also be explained by assuming the extracted species to be the simple lanthanum thiocyanate. The effect is again due to the extraction of the thiocyanic acid into the organic phase. The extracted thiocyanic acid is again presumed to ionize into hydrogen ions and thiocyanate ions, and it is this ionization which increases the concentration of "free" thiocyanate ions in the organic phase. The increase in "free" thiocyanate in turn represses any ionization of the lanthanum thiocyanate, and thereby represses further extraction of the lanthanum from the aqueous phase. These explanations of the effect of acidity were also used by Baldick (50a) for the extraction of ferric chloride into isopropyl ether.

The effect of increasing acidity is actually twofold, no matter which of the above mechanisms is correct. The second effect of the increasing acidity is the removal of thiocyanate ions from the aqueous phase into the organic phase by the extrac-

tion of the thiocyanic acid. This decrease in aqueous thiocyanate concentration also causes a depression in the amount of lanthanum which will cross the phase boundary, and thereby decreases the amount of lanthanum which will enter the organic phase.

It should be pointed out here that the large amount of thiocyanic acid which is extracted is an indication of one of four things, or a combination thereof:

(1) that thiocyanic acid is not as strong in aqueous solution as was previously believed,

(2) that it is a stronger acid in the tri-n-butyl phosphate than it is in water,

(3) that the partition coefficient for the undissociated acid is extremely high, or

(4) that the acid is more strongly solvated in tri-n-butyl phosphate than it is in water.

Variation of the Distribution Coefficient with Rare Earth Metal Used

In order to determine the possible usefulness of this extraction procedure for the separation of a mixture of rare earths, the distribution coefficients were measured for lanthanum, praseodymium, neodymium, and samarium under conditions as nearly identical as it was possible to make them. A graphical comparison is given as Figure 30 for the extraction of the rare earths from a 0.4 formal thiocyanate solution and for the extraction from perchlorate solution.

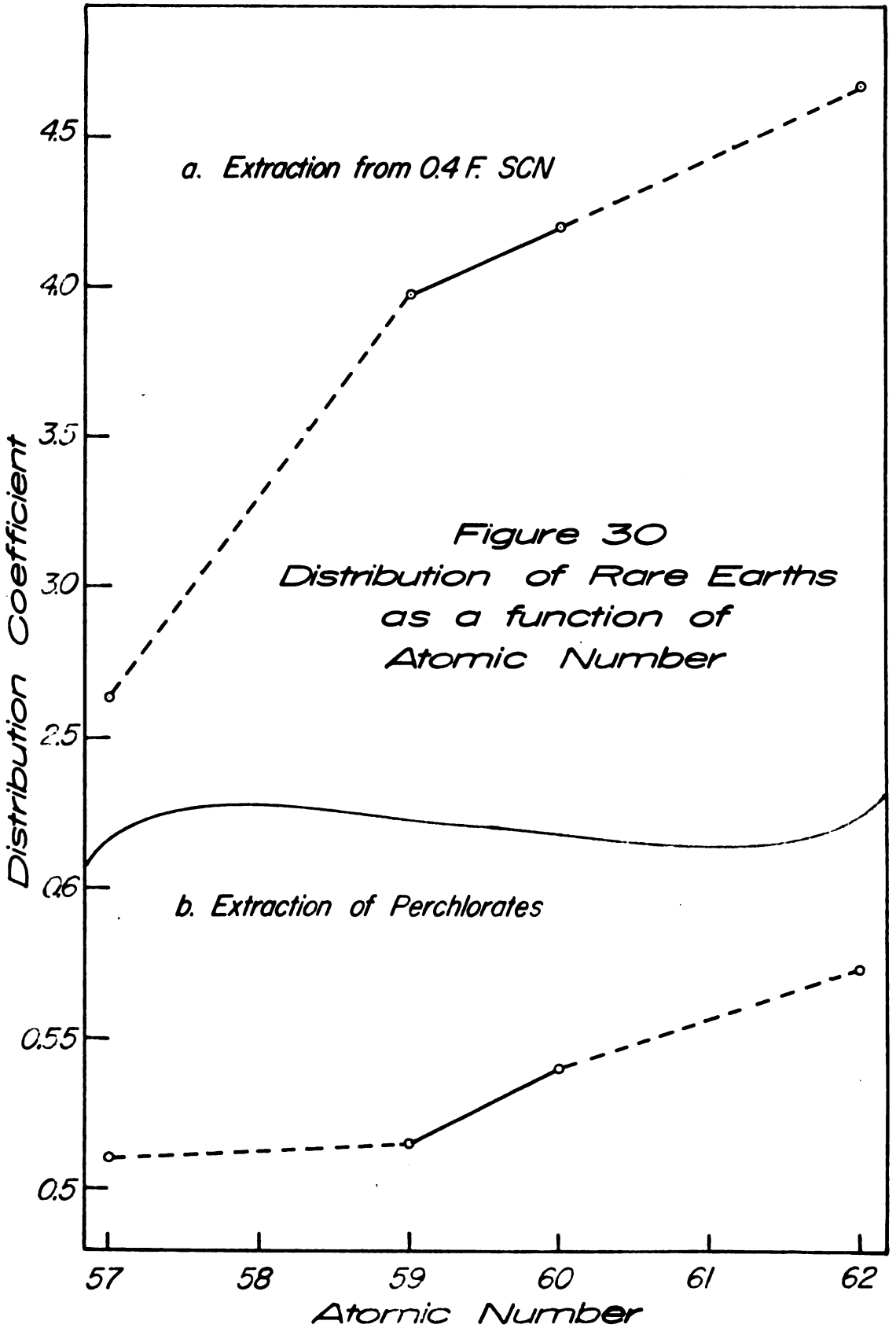

Figure 30
Distribution of Rare Earths
as a function of
Atomic Number

The differences between adjacent rare earths are not great for either of the conditions shown. There is a general trend, in that the distribution coefficients do increase with increasing atomic number. This trend is that which would be expected from the standpoint of basicities: that is, the less basic the rare earth ion involved, the more one would expect it to form ionic associations and therefore the more one would expect to be extracted by a non-aqueous solvent. The differences in the extraction of ammonium and sodium thiocyanate can also be ascribed to basicity differences.

Since the change in distribution coefficient as we change the rare earth is small, and since the change in extraction as the rare earth concentration is changed is great, it is probable that this system would not make a satisfactory separational procedure. It would be a most difficult task to calculate the distribution in a multi-stage extraction process, because the concentration of the rare earth, the thiocyanate ion, and the acidity would all vary from one stage to the next. The effect of temperature, however, is sufficiently small that it would not be necessary to control the temperature very rigidly during such a process, and if there were a small amount of iron introduced from the extraction equipment, the extraction would not be affected appreciably, as was shown by the experiment on the effect of a small amount of iron on the extraction of neodymium (see page 71).

Ceric cerium causes the decomposition of thiocyanate, and for

this reason, this system should be attempted for the separation of a mixture only if the majority of the cerium present in the mixture were removed beforehand.

A direct comparison of these extraction data with those in the literature is not possible because of the great variations in extractabilities when the condition of the extractions are changed. Separation factors also present no basis for comparison, since these vary as the initial ratio of one rare earth to another varies. The only comparison which may be given is that the distribution coefficients for the thiocyanates do appear to be greater than those of the nitrates obtained by Peppard et al. (46).

Spectral Changes in Neodymium Thiocyanate in Tri-n-butyl Phosphate Solution

As pointed out in the experimental section (pages 59 and 60), definite changes in the absorption spectrum of neodymium thiocyanate exist between an aqueous solution and a tri-n-butyl phosphate solution. Only a very slight change was observed in the tri-n-butyl phosphate solution of neodymium perchlorate from that in water. If the spectral changes described in the experimental section were caused by the formation of some sort of complex between tri-n-butyl phosphate and the neodymium, it does not seem reasonable that the neodymium would be more available for complexing with tri-n-butyl phosphate in the presence of thiocyanate than in the presence of perchlorate. In an attempt

to find a better explanation, the perchlorate solution in tri-n-butyl phosphate was placed in an oven at 110° C. to remove as much of the water dissolved in the solvent as possible, and the spectrum of this solution was compared with that previously recorded. The removal of the water resolved the absorption band in the region of 575 millimicrons to an even greater extent than that of the thiocyanate solution. It was then apparent that the major effect in the changes of the absorption spectrum is the removal of water from the atmosphere of the neodymium ion. This removal of water from the sphere of influence of neodymium should be easier if some material or ion were already present which had removed some of the water of co-ordination from the neodymium by replacement. Therefore, it seems that when neodymium thiocyanate is extracted into the tri-n-butyl phosphate it has less water of co-ordination than does the perchlorate. The thiocyanate, then, seems to have replaced some of the water co-ordinated to the neodymium ions. This, then, is additional evidence of the existence of some sort of association or complex between the rare earths and the thiocyanate ion.

SUMMARY

(1) Lanthanum, neodymium, praseodymium, and samarium thiocyanates were prepared, and their distribution between aqueous solutions and tri-n-butyl phosphate were studied.

(2) For each of the four rare earths used, and increase in the initial thiocyanate concentration was found to increase the distribution coefficient for the same initial acidity and metal concentration.

(3) The distribution coefficient for each of the rare earths studied was found to decrease as the initial metal concentration was increased if the initial thiocyanate concentration and acidity were maintained constant.

(4) The distribution coefficient was found to decrease as the initial acidity was increased if the initial metal and thiocyanate concentrations were kept constant.

(5) In studying the extraction of thiocyanate from aqueous sodium thiocyanate solution into tri-n-butyl phosphate, it was found that thiocyanic acid was the major species extracted.

(6) Extraction of lanthanum into the organic phase increased only slightly when the temperature of the extraction was increased from 25° C. to 35° C.

(7) The distribution of neodymium between the two phases was found to be unaffected by the presence of a small amount of iron in the solution.

(8) For the rare earths used, the distribution coefficient was found to increase with atomic number, or to decrease with increasing basicity.

(9) Evidence seems to indicate the existence of either an ion-pair type association or a complex compound between the rare earth and thiocyanate ions in each of the two phases.

(10) Any extraction studies making use of thiocyanate would have to be done on cerium free rare earth solutions because of the oxidizing action of tetravalent cerium. It is doubtful that cerium thiocyanate may be prepared.

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APPENDIX

Table XVIII

Contents of Solutions for Neodymium Extractions

Run No.	Ml. & F. $Nd(SCN)_3$	Formality $Nd(SCN)_3$	Ml. & F. $HClO_4$	Formality $HClO_4$	Ml. & F. NH_4SCN	Formality NH_4SCN	Ml. H_2O	Ml. T.B.P.
1	10(0.2)	0.10	10(0.202)	0.101	0	0	0	20
2	"	"	10(1.009)	0.504	0	0	0	20
3	"	"	10(2.018)	1.009	0	0	0	20
4	"	"	10(4.035)	2.017	0	0	0	20
5	"	"	5(0.404)	0.101	5(0.03560)	0.0089	0	20
6	"	"	"	"	5(0.178)	0.0445	0	20
7	"	"	"	"	5(0.356)	0.0890	0	20
8	"	"	"	"	5(1.780)	0.445	0	20
9	"	"	"	"	2(1.780)	0.178	3	20
10	"	"	"	"	3(1.780)	0.267	2	20
11	"	"	"	"	4(1.780)	0.356	1	20
12	20(0.143)	0.0715	10(0.404)	"	0	0	10	40
13	"	"	"	"	10(0.178)	0.0445	0	40
14	"	"	"	"	10(0.356)	0.0890	0	40
15	"	"	"	"	4(1.780)	0.178	6	40
16	"	"	"	"	6(1.780)	0.267	4	40
17	"	"	"	"	8(1.780)	0.356	2	40
18	"	"	"	"	10(1.780)	0.445	0	40
19	*20(0.086)	0.043	0	"	0	0	20	40
20	"	"	"	"	10(0.178)	0.0445	10	40
21	"	"	"	"	20(0.178)	0.0890	0	40
22	"	"	"	"	15(0.356)	0.1335	5	40
23	"	"	"	"	20(0.356)	0.1780	0	40

* This neodymium thiocyanate solution was prepared to be 0.2017 formal with respect to perchloric acid as well as being 0.0858 formal in neodymium.

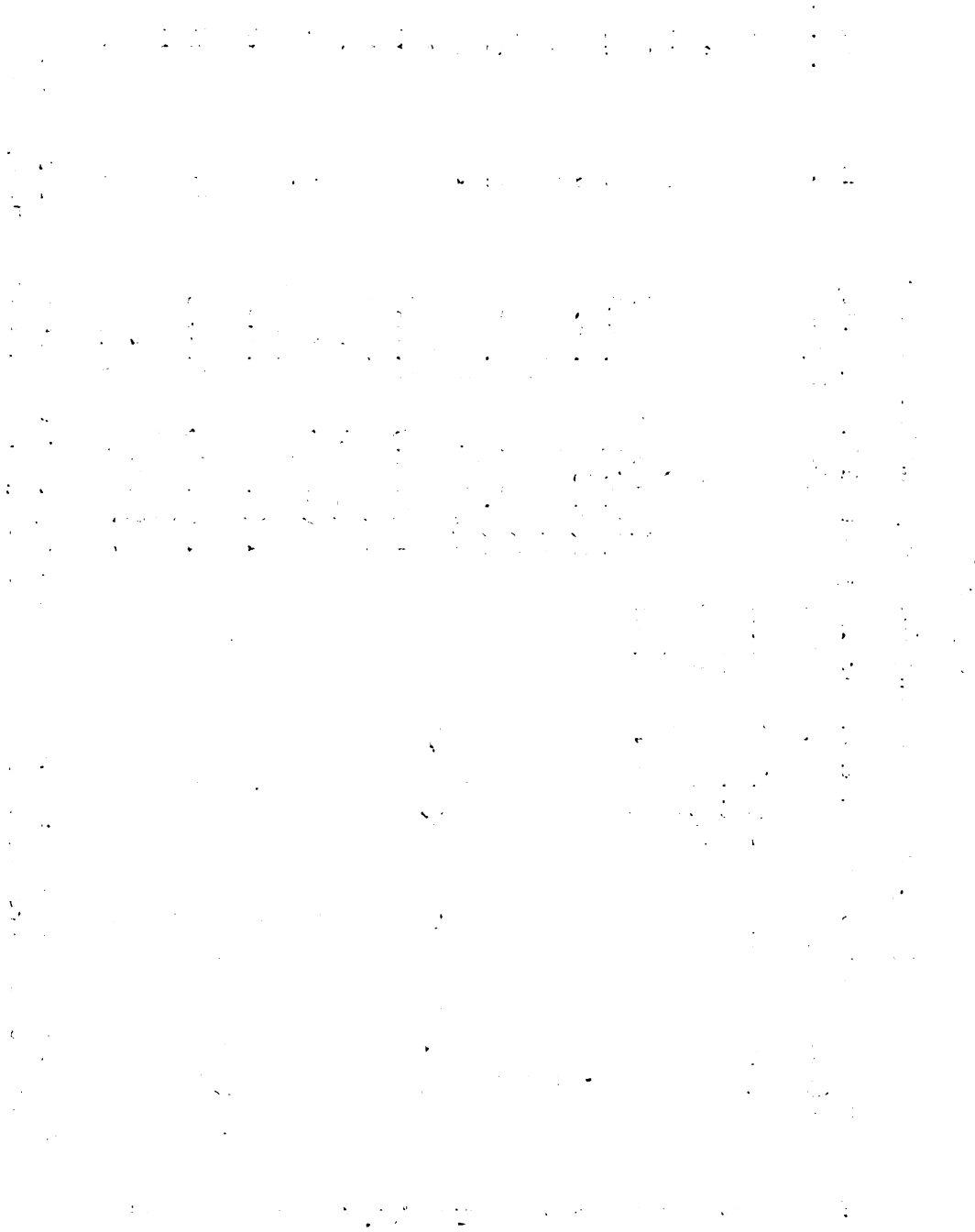

Table XIX

Analysis of Neodymium Solutions

Run No.	Sample Volume	Weight of Oxide from Aqueous: Sample I	Sample II	Sample III	Average	Weight of Oxide from Organic: Sample I	Sample II	Sample III	Average	Concentration: Aqueous	Organic
1	5	0.0455	0.0458	0.0462	0.0458	0.0400	0.0401	0.0418	0.0403	0.0545	0.0417
2	5	0.0728	0.0727	0.0723	0.0726	0.0217	0.0241	0.0225	0.0227	0.0773	0.0270
3	5	0.0860	0.0864	0.0867	0.0864	0.0096	0.0106	0.0104	0.0103	0.1028	0.0124
4	5	Not analyzed - There was no Nd absorption visible through the T.B.P. solution									
5	5	0.0459	0.0452	0.0455	0.0455	0.0434	0.0417	0.0419	0.0419	0.0541	0.0499
6	5	0.0396	0.0401	0.0401	0.0400	0.0461	0.0470	0.0469	0.0467	0.0477	0.0588
7	5	0.0351	0.0340	0.0346	0.0346	0.0520	0.0520	0.0505	0.0515	0.0412	0.0619
8	5	0.0084	0.0085	0.0089	0.0086	0.0775	0.0779	0.0788	0.0781	0.0102	0.0927
9	5	0.0238	0.0235	0.0228	0.0234	0.0640	0.0636	0.0615	0.0636	0.0280	0.0757
10	5	0.0163	0.0177	0.0157	0.0160	0.0705	0.0699	0.0696	0.0700	0.0190	0.0832
11	5	0.0114	0.0116	0.0118	0.0116	Ruined				0.0138	
12	10	0.0761	0.0761	0.0763	0.0761	0.0482	0.0469	0.0479	0.0479	0.0453	0.0285
13	10	0.0644	0.0643	0.0643	0.0643	0.0588	0.0580	0.0576	0.0580	0.0382	0.0345
14	10	0.0530	0.0526	0.0531	0.0530	0.0684	0.0686	0.0698	0.0686	0.0315	0.0408
15	10	0.0348	0.0339	0.0346	0.0347	0.0853	0.0845	0.0850	0.0850	0.0206	0.0506
16	10	0.0233	0.0242	0.0236	0.0237	0.0960	0.0961	0.0962	0.0961	0.0140	0.0572
17	10	0.0152	0.0143	0.0145	0.0147	0.1032	0.1031	0.1031	0.1031	0.0086	0.0613
18	10	0.0100	----	0.0097	0.0098	0.1069	0.1058	0.1061	0.1062	0.0058	0.0631
19	10	0.0554	0.0553	0.0553	0.0553	0.0185	0.0187	0.0184	0.0185	0.0329	0.0110
20	10	0.0451	0.0452	0.0456	0.0453	0.0283	0.0281	0.0281	0.0281	0.0269	0.0167
21	10	0.0462	0.0357	0.0362	0.0362	0.0374	0.0369	0.0368	0.0369	0.0215	0.0219
22	10	0.0272	0.0277	0.0265	0.0272	0.0448	0.0455	0.0447	0.0448	0.0162	0.0266
23	10	0.0213	0.0208	0.0215	0.0213	0.0514	0.0518	0.0515	0.0514	0.0127	0.0306

Table XX

Contents and Analysis of Neodymium Solutions

Run No.	Concentration of solution with respect to					Weight of Oxide from Organic				
	$Nd(SCN)_3$	$Nd(ClO_4)_3$	$HClO_4$	NaSCN	$NaClO_4$	Sample I	Sample II	Sample III	Average	Organic Conc Nd
24	0	0.1027	0.101	0	0.020	0.0584	0.0583	0.0586	0.0584	0.0695*
25	0.0667	0.0360	0.101	0	0.1698	0.0469	0.0468	0.0471	0.0469	0.0558
26	0.1027	0	0.101	0.0919	0.1507	0.0595	0.0598	0.0605	0.0598	0.0711
27	0.1027	0	0.101	0.2919	0.1063	0.0741	0.0739	----	0.0741	0.0882
28	0.1027	0	0.050	0.0919	0.300	0.0687	0.0693	0.0694	0.0693	0.0823
29	0.1027	0	0.202	0.0919	0.0902	0.0491	----	0.0489	0.0491	0.0584
30	0.1027	0	0.504	0.0919	0	0.0238	0.0238	0.0243	0.0238	0.0283
31	0	0.1027	0.101	0.400	0	0.0720	0.0719	0.0718	0.0719	0.0855
32	0	0.1027	0.101	0.600	0	0.0795	0.0796	0.0791	0.0794	0.0945
33	0	0.1027	0.050	0.400	0	0.0752	0.0753	0.0750	0.0752	0.0895
34	0.1027	0	0.101	0.0919	0	0.0658	0.0661	0.0660	0.0660	0.0785
35	0	0.1027	0.101	0.600	0	0.0792	0.0794	0.0795	0.0794	0.0945

*These data are for the aqueous phase, and not the organic phase.

Table XXI

Contents of Solutions for Lanthanum Extractions

Run No.	Ml. & F. $La(SCN)_3$	Formality $La(SCN)_3$	Formality $HClO_4$	Ml. & F. NH_4SCN	Formality NH_4SCN	Ml. H_2O	Ml. T.B.P.
1	10(0.2055)*	0.1027	0.101	0	0	10	20
2	"	"	"	5(0.356)	0.089	5	20
3	"	"	"	2(1.78)	0.178	8	20
4	"	"	"	3(1.78)	0.267	7	20
5	"	"	"	4(1.78)	0.356	6	20
6	"	"	"	5(1.78)	0.445	5	20
7	20(0.1370)*	0.0685	"	0	0	20	40
8	"	"	"	8(0.356)	0.071	12	40
9	"	"	"	15(0.356)	0.134	5	40
10	"	"	"	5(1.78)	0.223	15	40
11	"	"	"	7(1.78)	0.312	13	40
12	20(0.0799)*	0.0400	"	0	0	20	40
13	"	"	"	8(0.356)	0.071	12	40
14	"	"	"	20(0.356)	0.178	0	40
15	"	"	"	6(1.78)	0.267	14	40
16	"	"	"	9(1.78)	0.400	11	40

* These lanthanum thiocyanate solutions were prepared so as to be 0.2017 formal with respect to perchloric acid as well as being the formality stated with respect to lanthanum.

Table XXII

Analysis of Lanthanum Solutions

Run No.	Sample Volume	Weight of Oxide from Aqueous				Weight of Oxide from Organic				Concentration	
		Sample I	Sample II	Sample III	Average	Sample I	Sample II	Sample III	Average	Aqueous	Organic
1	5	0.0443	0.0447	0.0449	0.0447	0.0403	0.0406	0.0408	0.0406	0.0349	0.0498
2	5	0.0335	0.0333	0.0323	0.0333	0.0525	0.0516	0.0514	0.0516	0.0410	0.0632
3	5	0.0230	0.0336	0.0231	0.0231	0.0586	0.0597	0.0590	0.0590	0.0284	0.0724
4	5	0.0186	0.0176	0.0166	0.0176	0.0659	0.0655	0.0653	0.0655	0.0216	0.0805
5	5	0.0132	0.0143	0.0137	0.0137	0.0700	0.0717	0.0698	0.0700	0.0168	0.0858
6	5	0.0106	0.0119	0.0107	0.0107	0.0732	0.0740	0.0735	0.0735	0.0131	0.0902
7	10	0.0719	0.0716	0.0714	0.0716	0.0415	0.0412	----	0.0414	0.0440	0.0254
8	10	0.0552	0.0550	0.0546	0.0549	0.0583	0.0579	0.0572	0.0579	0.0337	0.0355
9	10	0.0423	0.0420	0.0423	0.0423	0.0695	0.0692	0.0694	0.0694	0.0260	0.0426
10	10	0.0284	0.0290	0.0293	0.0291	0.0826	0.0824	0.0823	0.0824	0.0179	0.0506
11	10	0.0198	0.0200	0.0192	0.0198	0.0905	0.0914	0.0913	0.0913	0.0122	0.0560
12	10	0.0508	0.0510	0.0509	0.0509	0.0155	0.0152	0.0152	0.0152	0.0312	0.0093
13	10	0.0376	0.0376	0.0370	0.0375	0.0278	0.0284	0.0282	0.0282	0.0231	0.0173
14	10	0.0167	0.0168	0.0167	0.0167	0.0323	0.0324	0.0319	0.0323	0.0102	0.0198
15	10	0.0132	0.0140	0.0136	0.0136	0.0513	0.0507	0.0514	0.0513	0.0084	0.0315
16	10	0.0062	0.0073	0.0069	0.0069	0.0577	0.0584	0.0580	0.0580	0.0042	0.0356

Table XXIII

Contents of Solutions for Lanthanum Extractions

Run No.	Ml. 0.279 F $La(SCN)_3$	Formality in $La(SCN)_3$	Ml. 0.279 F $La(ClO_4)_3$	Formality in $La(ClO_4)_3$	Ml. 0.404 F $HClO_4$	Formality in $HClO_4$	Ml. & F. NH_4SCN	Formality in NH_4SCN
17	0	0	10	0.1394	5	0.101	2.3 (1.78)	0.205
18	0	0	10	0.1394	5	"	3.4 (1.78)	0.303
19	0	0	10	0.1394	5	"	4.5 (1.78)	0.400
20	0	0	10	0.1394	5	"	2.8 (3.56)	0.498
21	0	0	10	0.1394	5	"	3.4 (3.56)	0.605
22	4.8	0.0669	5.2	0.0725	5	"	0	0
23	7.2	0.1004	2.8	0.0390	5	"	0	0
24	10	0.1394	0	0	5	"	0	0
25	10	0.1394	0	0	5	"	5.0 (0.356)	0.089
26	10	0.1394	0	0	5	"	2.3 (1.78)	0.205
27	5.86	0.0817	4.14	0.0577	5	"	3.09(0.356)	0.055
28	6.50	0.0906	3.50	0.0488	5	"	1.43(1.78)	0.127
29	6.94	0.0918	3.06	0.0476	5	"	2.36(1.78)	0.210
30	7.19	0.1002	2.81	0.0392	5	"	3.36(1.78)	0.299

Note: The total volume of the aqueous solution was made to be twenty milliliters in all cases. All solutions were equilibrated with twenty milliliters of tri-n-butyl phosphate.

Table XXIV

Analysis of Lanthanum Solutions

Run No.	Sample Volume	Weight of Oxide from Aqueous				Weight of Oxide from Organic				Concentration	
		Sample I	Sample II	Sample III	Average	Sample I	Sample II	Sample III	Average	Aqueous	Organic
17	5	0.0550	0.0548	0.0544	0.0548	0.0597	0.0598	0.0601	0.0598	0.0673	0.0734
18	5	0.0455	0.0456	0.0451	0.0454	0.0680	0.0682	0.0681	0.0681	0.0558	0.0836
19	5	0.0374	0.0376	0.0373	0.0374	0.0751	0.0754	0.0755	0.0754	0.0459	0.0926
20	5	0.0307	0.0310	0.0312	0.0310	0.0824	0.0829	0.0828	0.0827	0.0381	0.1016
21	5	0.0242	0.0242	0.0243	0.0242	0.0891	0.0886	0.0895	0.0891	0.0297	0.1094
22	5	0.0639	0.0635	0.0636	0.0635	0.0505	0.0507	0.0505	0.0505	0.0780	0.0620
23	5	0.0598	0.0596	0.0592	0.0595	0.0542	0.0542	0.0541	0.0542	0.0730	0.0665
24	5	0.0529	0.0529	0.0536	0.0531	0.0593	0.0592	0.0598	0.0594	0.0652	0.0728
25	5	0.0414	0.0420	0.0419	0.0419	0.0706	0.0710	0.0707	0.0708	0.0514	0.0869
26	5	0.0292	0.0296	0.0294	0.0294	0.0818	0.0826	----	0.0826	0.0361	0.1014
27	5	0.0559	0.0563	0.0561	0.0561	0.0575	0.0577	0.0581	0.0577	0.0689	0.0708
28	5	0.0461	0.0463	0.0459	0.0461	0.0670	0.0672	0.0675	0.0672	0.0566	0.0825
29	5	0.0356	0.0358	0.0354	0.0356	0.0763	0.0763	0.0768	0.0764	0.0437	0.0938
30	5	0.0278	0.0279	0.0278	0.0278	0.0841	0.0842	0.0845	0.0842	0.0341	0.1034

Table XXV

Contents of Solutions for Lanthanum Extractions

Run No.	Formality of the Solutions with Respect to: $La(SCN)_3$	$La(ClO_4)_3$	$HClO_4$	NH_4SCN	NaSCN	$NaClO_4$
31	0.0217	0.0810	0.101	0.135		
32	0.0331	0.0696	"	0.201		
33	0.0440	0.0587	"	0.268		
34	0.0584	0.0443	"	0.325		
35	0.0782	0.0245	"	0.365		
36	0	0.1027	"	0		
37	0.0155	0.0530	"	0.354		
38	0.0388	0.0297	"	0.384		
39	0.0622	0.0063	"	0.407		
40	0.0666	0.0018	"			0.279
41	0.0685		"		0.094	0.223
42	0.0685		"		0.194	0.159
43	0.0685		"		0.294	0.089
44	0.0685		"		0.394	0.012
45	0.0667	0.0360	"		0	0.170
46	0.1027		"		0.092	0.151
47	0.1027		"		0.192	0.208
48	0.0667	0.0727	"		0	0.0023
49	0.1333	0.0061	"		0	0.198
50	0.1394		"		0.182	0.169
51	0.1027		0.050		0.092	0.300
52	0.1027		0.101		0.092	0.235
53	0.1027		0.202		0.092	0.090
54	0.1027		0.504		0.092	0

Table XXVI

Analysis of Lanthanum Solutions

Run No.	Sample Volume	Weight of Oxide from Aqueous Sample I	Sample II	Sample III	Average	Weight of Oxide from Organic Sample I	Sample II	Sample III	Average	Concentration Aqueous	Organic
31	5	0.0410	0.0410	0.0409	0.0410	0.0432	0.0430	0.0433	0.0432	0.0503	0.0530
32	5	0.0327	0.0328	0.0326	0.0327	0.0510	0.0509	0.0504	0.0509	0.0401	0.0625
33	5	0.0234	0.0231	0.0239	0.0238	0.0600	0.0600	0.0601	0.0600	0.0293	0.0737
34	5	0.0191	0.0195	0.0195	0.0194	0.0630	0.0638	0.0637	0.0637	0.0238	0.0782
35	5	0.0152	0.0149	0.0155	0.0152	0.0677	0.0679	0.0680	0.0679	0.0187	0.0834
36	5	0.0551	0.0549	0.0548	0.0549	0.0282	0.0280	0.0279	0.0280	0.0674	0.0344
37	10	0.0222	0.0218	0.0217	0.0219	0.0861	0.0863	0.0861	0.0862	0.0134	0.0529
38	10	0.0170	0.0170	0.0173	0.0171	0.0943	0.0947	0.0944	0.0945	0.0105	0.0580
39	10	0.0129	0.0129	0.0134	0.0130	0.0985	0.0979	0.0984	0.0984	0.0080	0.0604
40	10	0.0339	0.0338	0.0336	0.0338	0.0778	0.0785	0.0784	0.0784	0.0207	0.0481
41	10	0.0249	0.0249	0.0246	0.0248	0.0871	0.0875	0.0868	0.0871	0.0152	0.0535
42	10	0.0178	0.0179	0.0178	0.0178	0.0944	0.0942	0.0942	0.0943	0.0109	0.0579
43	10	0.0123	0.0125	0.0124	0.0124	0.0994	0.0994	0.0993	0.0994	0.0076	0.0610
44	10	0.0085	0.0088	0.0087	0.0087	0.1031	0.1029	0.1031	0.1030	0.0053	0.0632
45	5					0.0501	0.0500	0.0498	0.0500		0.0614
46	5					0.0605	0.0606	0.0606	0.0606		0.0744
47	5					0.0695	0.0695	----	0.0695		0.0853
48	5	0.0635	0.0638	0.0638	0.0637					0.0782	
49	5					0.0759	0.0762	0.0758	0.0760		0.0933
50	5					0.0904	0.0905	0.0905	0.0904		0.1110
51	5					0.0658	0.0663	0.0662	0.0662		0.0813
52	5					0.0610	0.0610	0.0614	0.0610		0.0750
53	5					0.0469	0.0472	0.0467	0.0469		0.0576
54	5					0.0215	0.0218	0.0221	0.0218		0.0268

Table XXVII

Contents and Analysis of Praseodymium Solutions

Run No.	Concentration of Solution with respect to					Weight of Oxide from Organic				
	$Pr(SCN)_3$	$Pr(ClO_4)_3$	$HClO_4$	NaSCN	$NaClO_4$	Sample I	Sample II	Sample III	Average	Organic Conc Pr
1	0	0.1027	0.101	0	0.020	0.0574	0.0577	0.0574	0.0575	0.0678*
2	0.0667	0.0360	0.101	0	0.1698	0.0550	0.0550	0.0546	0.0549	0.0648
3	0.1027	0	0.101	0.0919	0.1507	0.0699	0.0696	0.0692	0.0696	0.0821
4	0.1027	0	0.101	0.2919	0.1063	0.0796	0.0803	----	0.0799	0.0943
5	0.1027	0	0.050	0.0919	0.300	0.0760	0.0760	0.0761	0.0760	0.0897
6	0.1027	0	0.202	0.0919	0.0902	0.0588	----	0.0584	0.0586	0.0691
7	0.1027	0	0.504	0.0919	0	0.0598	0.0597	0.0598	0.0598	0.0706*

* These data are for the aqueous phase, and not the organic phase.

Table XXVIII

Contents and analysis of Samarium Solutions

Run No.	Concentration of Solution with respect to $Sm(SCN)_3$	$Sm(ClO_4)_3$	$HClO_4$	NaSCN	$NaClO_4$	Weight of Oxide from Organic Sample I	Sample II	Sample III	Average	Organic Conc Sm
1	0	0.1027	0.101	0	0.020	0.0570	0.0569	0.0569	0.0569	0.0653*
2	0.0667	0.0360	0.101	0	0.1698	0.0580	0.0579	0.0580	0.0580	0.0665
3	0.1027	0	0.101	0.0919	0.1507	0.0738	0.0738	0.0738	0.0738	0.0846
4	0.1027	0	0.101	0.2919	0.1063	0.0820	0.0826	0.0824	0.0823	0.0944
5	0.1027	0	0.050	0.0919	0.300	0.0796	0.0790	0.0793	0.0793	0.0909
6	0.1027	0	0.202	0.0919	0.0902	0.0612	0.0615	0.0610	0.0612	0.0702
7	0.1027	0	0.504	0.0919	0	0.0593	0.0592	0.0596	0.0593	0.0680*

* These data are for the aqueous phase, and not the organic phase.

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