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ANION EXCHANGE SEPARATIONS OF THE
RARE EARTHS IN NONAQUEOUS SOLVENTS

by

Richard George Greene

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INTRODUCTION

Anion exchange column chromatography has become an important analytical tool since Sussman *et al*. (1) in 1945 suggested the use of anion exchange in connection with the recovery of metals. This technique was perhaps highlighted by the work of Kraus and Nelson (2,3), who in 1948 made the first complete study of the behavior of metal ions on a strongly basic anion exchange resin. They studied the sorption or distribution coefficients of most metals over a range of 0.1 to 12M hydrochloric acid.

Over the past few years many other inorganic ligands have been used for anion exchange separations. The most popular ones are fluoride, bromide, iodide, cyanide, thiocyanate, nitrate, sulfate, and phosphate. Some of these, such as bromide, can be used effectively to separate many different metals while others, such as nitrate, have in the past been used with only a few particular metals. This is simply because bromide forms strong complexes with more metals than does nitrate. However, since the advent of organic solvents in the ion exchange field, this consideration has become less important. The reason for this is that the replacement of water by appropriate organic solvents promotes the formation of metal complexes. Thus a metal that does not form a complex with a particular ligand in water often does so in an organic solvent or in a mixed water-organic solvent. The organic solvents most commonly used are the lower alcohols, acetone, dioxane, and acetic acid.

A good reason for studying the rare earths is their growing industrial importance in addition to their common occurrence as a result of nuclear reactions. For industrial uses they are taken mainly from the mineral monazite. Of the purified elements, only cerium, lanthanum, and a low-cerium mixture known as didymium are produced in ton quantities. Scandium, gadolinium, europium, dyprosium, and erbium are of interest in atomic energy development because of their neutron-absorption characteristics. Yttrium has the possibility of being used as a structural metal and as a fuel matrix material. Yttrium and gadolinium are used in garnets as low-loss magnetic components for microwave circuitry. Compounds such as cerium sulfide and gadolinium selenide may become useful for thermoelectric power generation. There are many other miscellaneous applications for the rare earths. Neodymium and praseodymium are used for coloring glass and enamel. Highly purified lanthanum is put in a special glass for the manufacture of instrument and camera lenses. Misch metal, made from the rare-earth chloride, is alloyed with iron and used in the manufacturing of lighter flints. Rare-earth fluoride and oxide in carbon electrodes, used for arc illumination, provide a very high light intensity and give a stable arc. The addition of rare earths to certain alloys gives superior high temperature properties and increases service life.

EXPERIMENTAL

Apparatus

Laboratory ware

The ion-exchange columns used were 27 cm. in length. The lower portion of a column, 16 cm. long and with an inside diameter of 1.2 cm., held the resin by means of a coarse glass frit. The top part of the column was 11 cm. long with an inside diameter of 1.8 cm. In one case a column of approximately 50 cm. length with an inside diameter of 0.5 cm. was used. The flow rate was controlled with a two-way polyethylene stopcock. A 125 ml. separatory funnel, fitted with a rubber stopper and placed on top of the column, served as a reservoir for the eluting solvent. Kimble "Nomax" burettes and Kimble "Exax" pipettes were used throughout this work.

pH meter

All pH measurements were made on a Beckman Model G pH meter equipped with a Beckman 1190-80 glass electrode and a Beckman 1170 calomel electrode.

Spectrophotometers

A Beckman Model B or a Cary Model 14 spectrophotometer were used for all spectrophotometric measurements.

Stirrer

A Burrell shaker was used in the equilibration of samples for distribution studies.

Reagents

Ion-exchange resin

J. T. Baker Chemical Company "Analyzed Reagent" grade Dowex 50W-X8, 100-200 mesh catión-exchange; Dowex 1-X8, 20-50 mesh anion exchange; and Rohm and Haas Company Amberlyst XN-1002 anion exchange resins were used. The Amberlyst resin was ground to 60-100 mesh before using. The cation-exchange resin was regenerated as follows: About 300 grams of the resin in a large diameter column (8.5 cm.) was first back-washed with distilled water to remove any fine particles. The resin was then washed with three liters of 10% ammonium citrate to remove metal ions. Then it was converted to the hydrogen form by washing with three liters of 3M hydrochloric acid. Finally the resin was washed with distilled water until a negative test for chloride was obtained with silver nitrate. It was then sucked partially dry, spread onto filter paper, and allowed to dry further in the air for 24 hours. The anion-exchange resin was also first washed. It was then purified by washing first with two liters of 0.1M hydrochloric acid. The resin was converted to the nitrate form by washing with 3M nitric acid until a negative test was obtained for chloride. The resin was then washed with distilled water and allowed to dry, as with the catex resin. For column experiments the air-dried resin was soaked in the eluting solution prior to its addition to the column. The ion exchange column was also prepared by adding the resin to the column from an aqueous solution and then passing two to three column volumes of the eluting solution through the column.

EDTA [disodium dihydrogen (ethylenedinitrilo) tetraacetate dihydrate]

The EDTA was Baker Chemical Company "Analyzed Reagent".

Metal ion solutions

Stock solutions of the elements used were prepared 0.05M in metal ion. The rare earth solutions were prepared by dissolving their oxides in approximately 8M nitric acid and diluting the resultant solutions to 0.5M in nitric acid. Most other elements were prepared from their nitrate salts into dilute nitric acid. Titanium(IV) and vanadium(IV) solutions were made up in dilute sulfuric acid. Zirconium(IV) was used in perchloric acid solution.

Organic solvents

J. T. Baker acetone, methyl alcohol, and isopropyl alcohol were used.

Organic solvent-water-nitric acid mixtures

The mixtures were made up adding concentrated nitric acid and water to the approximate amount of organic solvent needed and then diluting to the mark in a volumetric flask with the organic solvent. The mixtures were expressed as percent by volume or organic solvent and molarity (M) of nitric acid. If 10 ml. of 1M nitric acid were added to methyl alcohol and then more methyl alcohol added to bring the volume to 100 ml., the resultant solution would be 90% in methyl alcohol and 0.1M in nitric acid. This approach ignores the fact that because of a volume shrinkage more than 90 ml. of methyl alcohol would be present.

Analytical Procedures

EDTA

EDTA solutions were standardized by titrating a standard zinc(II) solution using Naphthyl Azoxine S(NAS) as the indicator as described by Fritz *et al.* (4).

Magnesium(II)

Magnesium was analyzed by a direct titration with EDTA using Eriochrome Black T indicator as described by Bernard, Broad, and Flaschka (5).

Calcium(II)

Calcium was determined by back titration with magnesium using Eriochrome Black T indicator as described by Bernard *et al.* (5).

Strontium(II)

Strontium was analyzed by titration with EDTA using metalphthalein indicator as described by Bernard *et al.* (5).

Titanium(IV), vanadium(IV), iron(III), indium(III), aluminum (III) and tin(IV)

These elements were analyzed by back titration with copper after addition of excess EDTA using Naphthyl Azoxine S indicator as described by Fritz *et al.* (4).

Scandium(III), yttrium(III), rare earths(III), cobalt(II) and gallium(III)

These metals were analyzed by back titration with copper at pH 5-6 after addition of excess EDTA using Naphthyl Azoxine S indicator. Pyridine was used as the buffer.

Manganese(II)

This analysis was performed by a direct titration with EDTA using Eriochrome Black T indicator in the presence of ascorbic acid and cyanide. (6, p. 217)

Nickel(II), copper(II), zinc(II), cadmium(II), and lead(II)

These elements were analyzed by direct titration with EDTA using NAS indicator. (4)

Bismuth(III) and zirconium(IV)

Analysis of these elements was performed with EDTA using Xylenol Orange indicator as described by Körbl and Pribil. (7)

Mercury(II)

Mercury was determined by titration with thioglycerol (1-mercaptopropane-2,3-diol) solution at pH 6 using thio-Michler's ketone indicator.

Nitrate

This analysis was performed spectrophotometrically at 300 mu using a Cary Model 14 Spectrophotometer.

Manganese(II)

Small quantities of manganese were determined by the periodate method given by Vogel (8).

Lanthanum(III) and ytterbium(III)

These elements were determined using Arsenazo by the method of Fritz *et al*. (9).

Measurement of Distribution Coefficients

In developing separation procedures by ion exchange, the most efficient approach is usually through the determination of distribution coefficients. This is because there are often several variables to be considered such as choice of proper ligand, concentration of ligand, and choice of solvent. Systematic measurements of distribution coefficients make it possible to correlate these variables and enable the investigator to choose quickly the best conditions for separations. This approach also has the advantage that distribution coefficients can be related to the size of column needed for the particular separation desired.

Distribution coefficients can be determined by batch or column methods. The batch method was used in this work because it is better suited for the handling of a large number of samples.

The units usually chosen for distribution coefficients are amount of metal per gram of dry resin and amount of metal per milliliter of solution. The batch distribution coefficient, D, can then be computed according to Equation 1:

$$D = \frac{\text{millimoles of metal on resin/gram of dry resin}}{\text{millimoles of metal in solution/ml of solution}} \qquad (1)$$

The batch distribution coefficient, D, is related to the volume distribution coefficient, D_V, by the following equation:

$$D_V = D\rho \tag{2}$$

where ρ is the bed density (grams of dry resin per ml. of resin bed). The quantity ρ can be determined by measuring the volume of a settled wet column containing a known weight of dry resin. D_V can then be related to the volume of eluent required to elute the constituent to its elution maximum on the Gaussian elution curve by the following equation:

$$V = Ad\ (D_V + i). \tag{3}$$

In this equation V is the volume of eluent (ml.) which moves a band maximum d (cm.) in a column of cross sectional area A (sq. cm.) and fractional interstitial volume i. From this equation then, one can get a good estimate of the volume of eluting solution needed to elute a substance from any particular size column.

In comparing the preference of an ion exchanger for two counter ions, the separation factor, α^A_B, is the quantity utilized. It is defined:

$$\alpha^A_B = \frac{D_A}{D_B}\ . \tag{4}$$

Distribution coefficients were determined as follows: The amount of dry resin used was calculated from the amount of air-dried resin used. The moisture content of the air-dried resin was determined by weighing a sample of resin before and after heating in an oven to constant weight at

110°C. Approximately 0.5 to 1 gram of the air-dried resin was accurately weighed into a 125 ml. ground glass stoppered Erlenmeyer flask. Fifty ml. of the appropriate solvent mixture containing the metal ion being investigated was then pipetted into the flask. The flask was stoppered and shaken on the Burrell shaker until equilibrium was attained. With organic solvents from four to 16 hours was taken to insure the reaching of equilibrium. An aliquot was then withdrawn and the metal ion determined by a titrimetric or occasionally a colorimetric method.

Column Separation Procedure

In preparing an ion-exchange column, the resin was first slurried in a beaker with the solvent being used. This was added to a glass column to the desired height. Usually column heights of from 12 to 16 cm. were used. Between two to three column volumes of the solvent were then passed through to insure the reaching of equilibrium and also to help settle the resin. The metal ion sample was prepared by pipetting between 0.05 to 0.25 mmole of a metal ion from an aqueous stock solution into a 10 ml. beaker. This solution was evaporated just barely or almost to dryness. Then either the eluting solvent or three to four drops of dilute nitric was added to bring the residue into solution. Three to five ml. of the eluting solution was added to the beaker and this was poured onto the top of the ion exchange colunn. The beaker was then washed thoroughly with additional eluting solution to give a total volume in the reservoir of the column of about 10-12 ml. This was allowed to pass through the column at a flow rate of 0.25 to 0.50 ml. per minute. The eluting solvent was then added dropwise from the attached separatory funnel. Care was taken at this point not to disturb the top of the resin bed with the eluting solvent. In the separation of two metal ions, following the elution of the first metal the column was washed with dilute nitric or perchloric acid to elute the second metal. Most elutions were carried out with a flow rate of about 0.5 ml. per minute through the column. With some easily separable metals, the flow rate was increased up to 0.9 ml. per minute. In the separation of vanadium(IV) following the evaporation of the sulfate solution to near dryness and after three to four drops of dilute nitric acid had been added, some solid ascorbic acid was added to make sure vanadium was in the quadrivalent state.

Determination of Invaded Nitrate

In the invasion experiments the amount of invasion (sorption of significant quantities of electrolyte) in anion exchange resin was determined by measuring the concentration of nitrate in the resin phase after equilibration with a solution of known electrolyte concentration.

One gram of resin was equilibrated with the solution by passing about 150 ml. of the solution through an ion exchange column of the type used throughout this work at a flow rate of about one ml. per minute. Interstitial and excess liquid trapped in the column were forced out by blowing at the top of the column for between five to 10 seconds. Blowing for periods much longer than this could result in the solution inside the resin beads being forced out. After this step the inside walls of the column were wiped free of adhering liquid. Finally the solution in the resin beads was washed out with about 25 ml. of water into a volumetric flask. An acid should not be used for this purpose, since it would displace the nitrates held by the resin sites. The nitrate concentration was then determined spectrophotometrically.

SEPARATION OF THE RARE EARTHS FROM OTHER METAL IONS

Survey of the Literature

In the late 1950's and early 1960's a number of investigators (3,10,11,12,13) deomonstrated that sorption of rare earths from aqueous mineral acid on anion exchange resin was small. When the nitrate system was investigated by these researchers and others (14,15), it was found that rare earth sorption was better although still weak.

In 1961, Korkisch and Tera (16), who with their coworkers had been studying ion exchange in mixed solvents, worked out a method for separating thorium from the rare earths and other metals. They made use of the strong sorption of thorium from a solution consisting of 90% methanol and 10% 5M nitric acid. The rare earths also were shown to sorb fairly strongly on the anion exchange resin.

Faris and Warton (17) worked with various mixtures of methanol and nitric acid in studying the sorption of the rare earths on anion exchange resin. They determined conditions for separating the rare earths from each other using these solvent mixtures.

Korkisch _et_ _al_. (18) studied various alcohols with the rare earths in nitric acid. They determined the distribution coefficients of various metals in different solvent mixtures and proposed a separation scheme for separating the rare earths from a few other metals.

Korkisch and Arrhenius (19) studied the separation of uranium, thorium, and the rare earths from other metals. They used a medium consisting of 90% glacial acetic acid and 10% 5M nitric acid to sorb these metals on anion exchange resin. Until these investigators had published their research, no method for separating the rare earths from a large number of metals by anion exchange techniques had appeared in the literature. The work in this thesis on separating the rare earths from other metals was performed, and a paper published (20), at about the same time as that of Korkisch and Arrhenius. Comparison experiments to be discussed later showed that the method discussed in this thesis has some important advantages over the aforementioned work.

Conditions for Separations

Preliminary experiments and previous research (18) showed that the rare earths are more strongly sorbed onto an anion exchange column (nitrate form) from aqueous isopropyl alcohol solutions containing nitric acid than from solutions containing a lower alcohol. The higher distribution coefficients in isopropyl alcohol can at least partially be attributed to the lower dielectric constant of this solvent. It has been generally accepted that the lower the dielectric constant of a solvent the stronger are the interactions between metal ions and ligands present in it. These stronger interactions then increase the tendency for neutral and anionic species to be formed from lower species. As a result more of a metal will enter the resin phase, giving higher distribution coefficients. A correlation between dielectric constant and distribution coefficient has been shown by Korkisch (21). His data have been reproduced in Table 1. It can be observed from this table that the distribution coefficients in quite a few instances do not vary as would be predicted from the dielectric constants. Thus to be completely correct, more than the dielectric constant would have to be considered in predicting how distribution coefficients would vary with different solvents.

Table 1. Variation of distribution coefficients and dielectric constants in different solvents using 90% organic solvent-10% 5M HNO_3

Solvent	Metal ion			Dielectric constant
	Cd	Zn	Al	
Water	1	1	1	80
Methyl alcohol	5	1	1	32.6
Ethyl alcohol	14	1	1	24.3
Acetone	57	12	37	21.4
n-propyl alcohol	42	8.5	4.4	20.1
Isopropyl alcohol	95	16	2.6	18.3
Isobutyl alcohol	71	35.5	17	17.7
n-butyl alcohol	42	21	11.3	17.1
Acetic acid	83	8.2	1	7.1

Another factor to be considered is the decrease in distribution coefficients that results when an increase is made in the amount of metal ion being equilibrated with the resin. With anion exchange a possible cause for this decrease could be the decreasing concentration of counter ion in the resin phase as the concentration of the metal in the solution is increased. Increasing the concentration of metal in the solution results in an increase in the metal complex concentration in the resin. Since metal complexes entering the resin phase undergo further complexation, additional nitrates have to be available in the resin. Obviously a point is eventually reached at which there are not enough counter ions available to cause further complexation to take place with the complexes entering the resin. The following reaction would then be shifted to the left.

$$M(NO_3^-)_{3(r)}^{0} + NO_{3(r)}^{-} = M(NO_3^-)_{4(r)}^{-} \qquad (5)$$

The symbol (r) after a species means the reaction is taking place in the resin phase. The neutral species would then distribute themselves between the resin and solution phase, thus lowering the distribution coefficient. In Figure 1, it can be seen that the distribution coefficients for ytterbium(III) fall quickly after a load of 0.1 mmoles per gram has been reached. This indicates that amounts no larger than 0.1 mmoles per gram should be used for this type of system in determining distribution coefficients. The curve also indicates that loading could be a significant problem when working with column separations in this system. When column separations were actually performed later in this work, this hypothesis was confirmed.

It is a general rule that rates of reaching equilibrium are slower in organic solvents than in water. The main

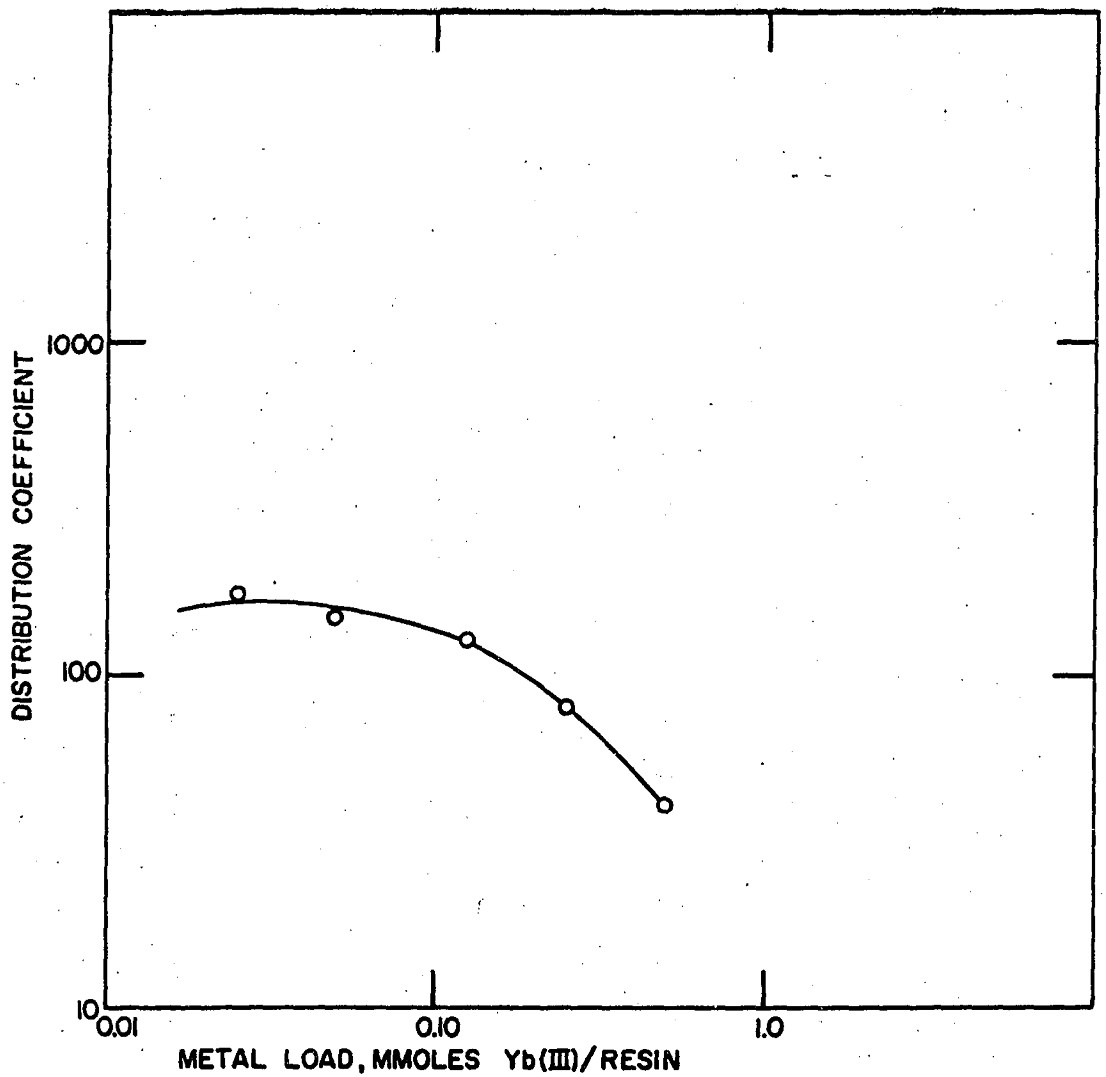


Figure 1. Variation of distribution coefficients with load using 0.5M nitric acid-95% isopropyl alcohol

reasons for this can be attributed to the generally lower viscosity of organic solvents and the lower mobility of counter ions in the resin. Lower mobility results when the resin swells less than in water. This makes movement throughout the resin more difficult. Lower mobility also results from the stronger interactions with the functional groups of the resin. This is due to the lower dielectric constant of organic solvents. Since it is usually desirable to compare distribution data under equilibrium conditions, experiments were performed to establish the time needed for equilibrium to be attained in a typical mixed solvent system. Sorption rate experiments with Dowex-1-X8 resin and Amberlyst XN-1002 were performed to compare the rates of reaching equilibrium. A resin in which the rate of attaining equilibrium is rapid allows the use of fast flow rates when column separations are being performed. From Figure 2, it can be seen that the Amberlyst resin is superior in this respect.

This superiority of the Amberlyst resin is probably due to it being a macroreticular type ion-exchange resin. This type has wide pores up to several hundred angstrom units, which allows easy access to the interior of the resin particle.

Isopropyl alcohol was chosen as the solvent to be used in separating the rare earths from other metals because it was thought that the comparatively higher distribution coefficients in this solvent might facilitate the separations. This turned out to be the case because, even though the

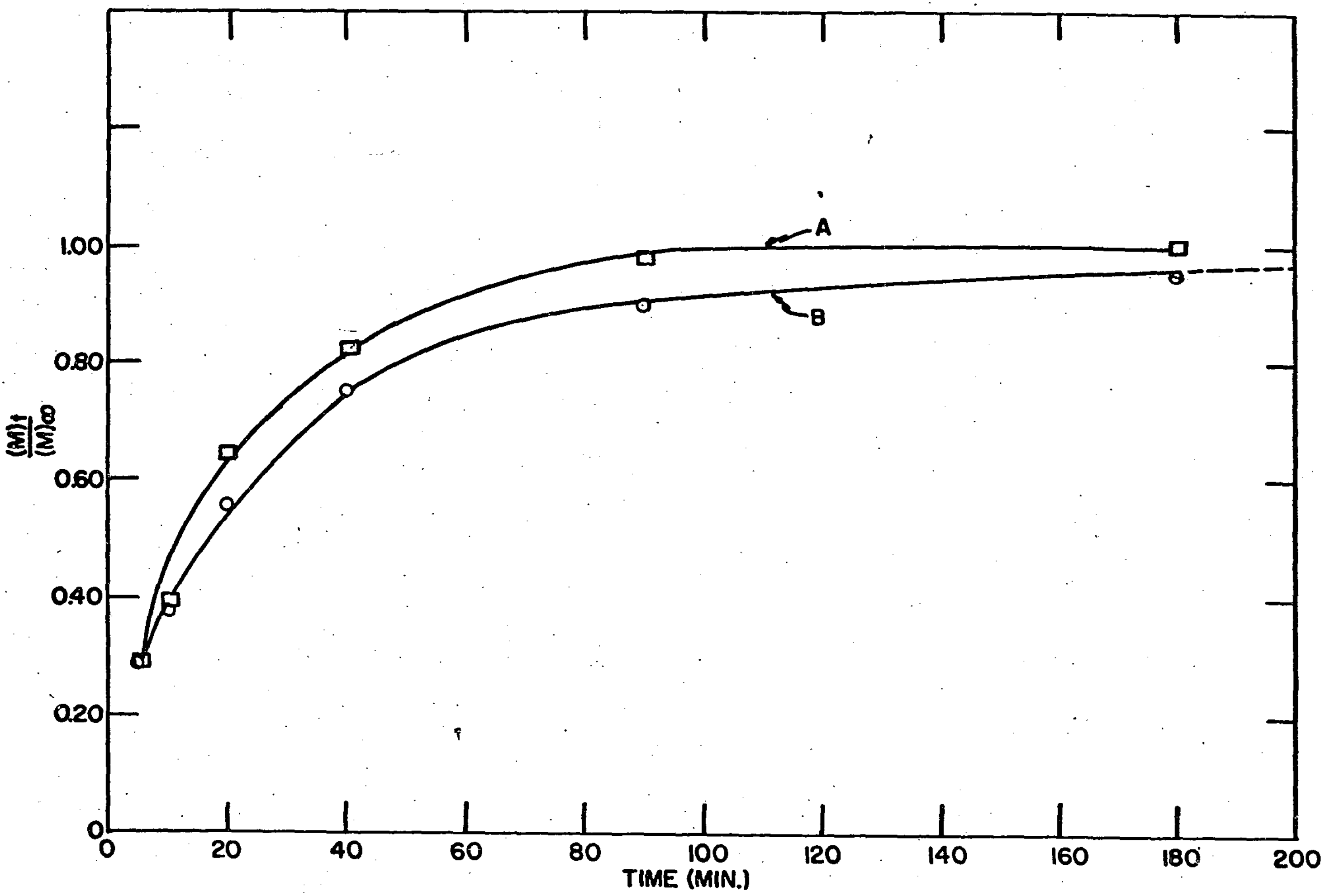
Figure 2. Sorption rate experiment in 1.5M nitric acid-85% isopropyl alcohol

A. Amberlyst XN-1002

B. Dowex 1-X8

M_∞ is the sorbed amount of metal at equilibrium

M_t is the sorbed amount of metal at time t


A
B
1.00
0.80
0.60
0.40
0.20
0
$\frac{(M)_t}{(M)_\infty}$
0
20
40
60
80
100
120
140
160
180
200
TIME (MIN.)

distribution coefficients of the rare earths were high, the distribution coefficients of many other metals remained relatively low. In attempting to find the best percentage of alcohol and concentration of nitric acid to use, three main factors were considered: 1) At high percentages of alcohol rates of attaining equilibrium become slower. 2) Nitric acid reacts with the alcohol when its concentration is too high. 3) The distribution coefficients of the rare earths drop fairly rapidly as the percentage of alcohol is lowered. Considering these points and using the data in Figure 3, it was decided to use a solution of 1.5M nitric acid in 85% isopropyl alcohol.

Results and Discussion

In agreement with previous work (17,18) it was found that the batch distribution coefficients decrease with increasing atomic weight of the rare earths (Figure 4). This is explained by the increasing hydrated radius of the rare earths with increasing atomic weight. As a result the interaction between the rare earth and a ligand will decrease with an increase of atomic weight, leading to lower distribution coefficients. The lower rare earths are held tightly by an anion exchange column but in some experiments the higher rare earths showed a tendency to break through before a column separation was complete. This was explained by the sensitivity of this system to loading, as can be seen from Figure 1 and Table 2. Thus a suc-

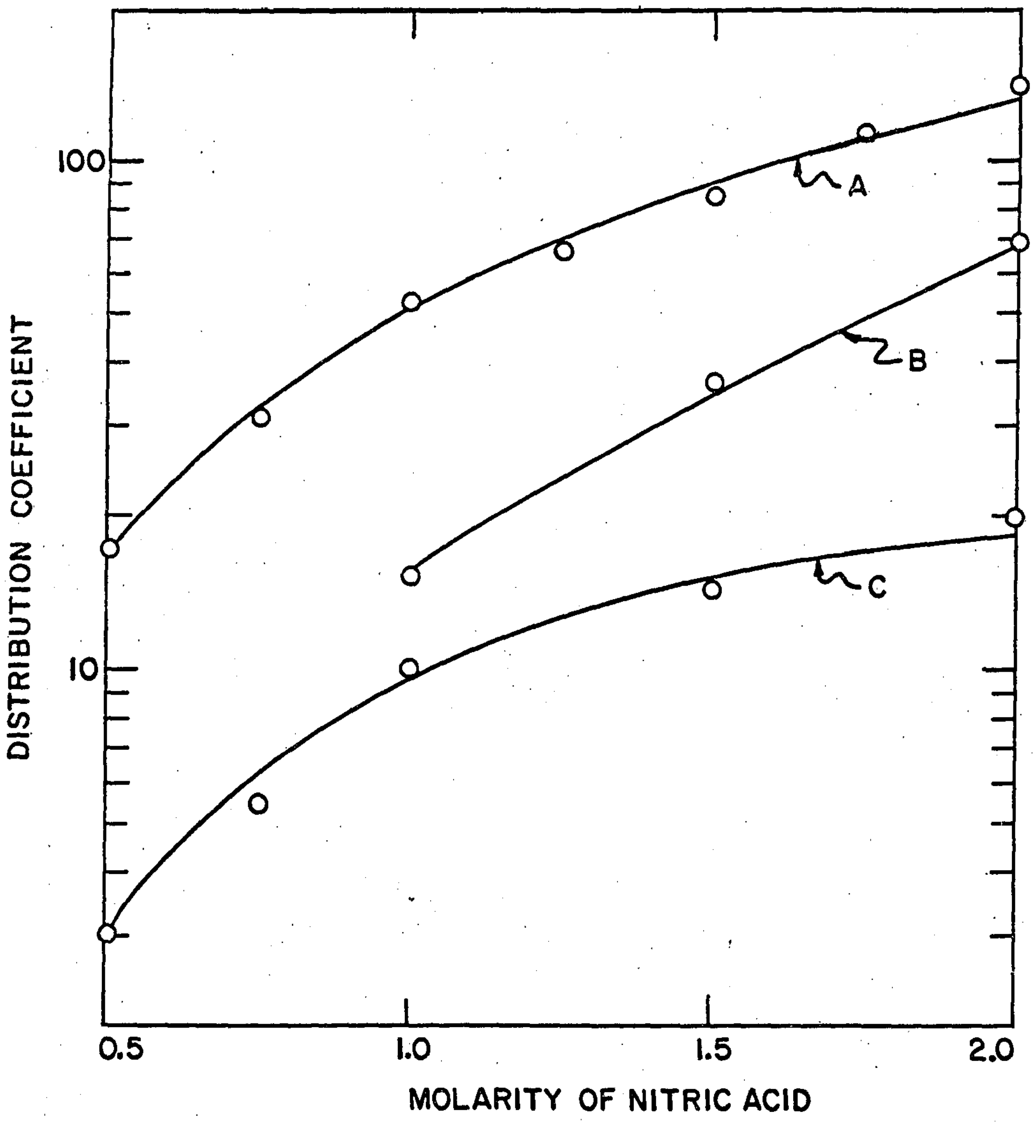


Figure 3. Distribution coefficients of ytterbium(III) and copper(II) as a function of nitric acid concentration

A. Ytterbium(III) in 85% isopropyl alcohol
B. Ytterbium(III) in 80% isopropyl alcohol
C. Copper(II) in 85% isopropyl alcohol

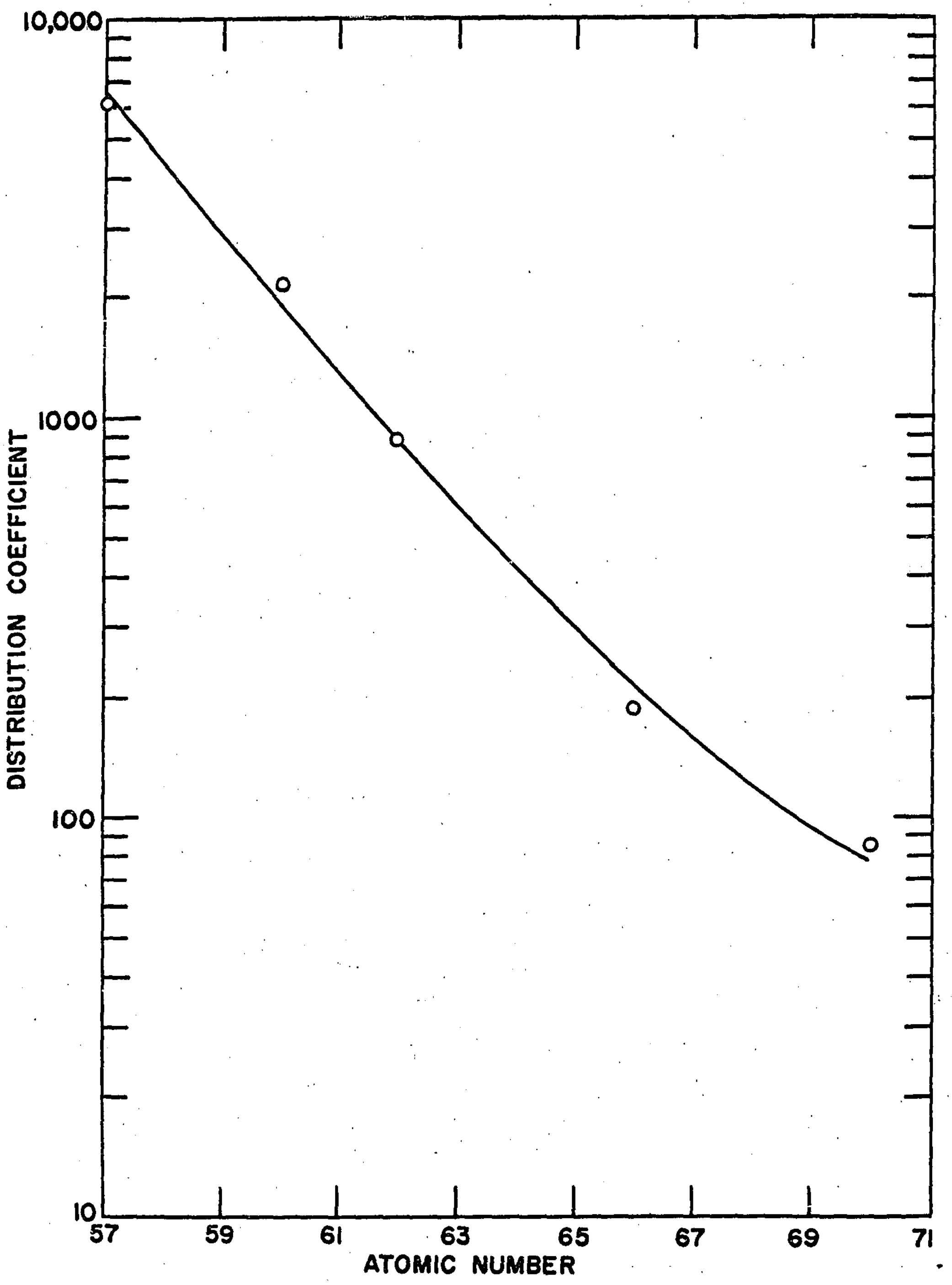


Figure 4. Distribution coefficients of the rare earths on Amberlyst XN-1002 anion-exchange resin in a solution of 1.5M nitric acid-85% isopropyl alcohol

cessful separation of rare earths from other metals is facilitated by selection of sample size so that a rather small amount of the higher rare earths is present.

Table 2. Column loading experiment using 1.5M HNO_3-85% isopropyl alcohol
(Flow rate 0.5 ml./min.)

Column length	Mmole ytterbium(III)	Breakthrough volume, ml.
16 cm.	0.0057	350
	0.10	310
	0.20	230
	0.30	130
	0.35	120
12 cm.	0.10	215
8 cm.	0.25 mmole La(III)	200

Data for the batch distribution coefficients and the volumes required for column elution of the elements studied are summarized in Table 3. Using a 1.2 x 16 cm. column, elements having a batch distribution coefficient of 10 or less can be quantitatively separated from 0.25 mmoles or less of the higher rare earths and probably from a somewhat larger quantity of the lower rare earths. The only exception in Table 3 is the titanium(IV) peroxide complex. This species tails somewhat on a column and also forms a precipitate when the eluting solvent mixture is added to a beaker containing titanium(IV) and more than 0.005 mmoles of rare earth. In order to achieve a quantitative separation of these metals, 0.10 mmoles of titanium(IV) and about 0.005 mmoles of ytterbium(III) were first evaporated to just dryness. They were

Table 3. Distribution coefficients and elution volumes in 1.5M HNO_3-85% isopropyl alcohol on Amberlyst XN-1002

Metal ion	Distribution coefficients $\frac{0.1\text{ mmole metal}}{50\text{ ml.}}$ load	Elution volume, 16 cm column 0.25 mmole load
Mg(II)	2.3	75
Ca(II)	56	--
Sr(II)	187	--
Y(III)	85	--
Zr(IV)	16	--
Ti(IV) with H_2O_2	9.9	180(12 cm column)
Ti(IV) with H_2O_2	9.9	220
V(IV)	6.7	100
V(V)	15	200
Mn(II)	6.7	130
Fe(III)	3.3	120(12 cm column)
Fe(III)	3.3	140
Co(II)	5.8	110
Ni(II)	5.4	110
Cu(II)	14	175(12 cm. column)
Zn(II)	3.2	110
Cd(II)	65	---
Hg(II)	228	---
Ag(I)	17	---
Al(III)	2.6	120
Ga(III)	3.8	130
In(III)	9.1	150
Pb(II)	1100	---
Bi(III)	1300	---
Yb(III)	85	---
Dy(III)	180	---
Sm(III)	866	---
Nd(III)	2200	---
La(III)	5900	---

then brought back into solution by the addition of three drops of hydrogen peroxide and two drops of dilute nitric acid, followed by the addition of 3-4 ml. of the eluting solvent mixture. This solution was put on a 12 cm. column of resin. The total volume of solution on the resin was, after washings, about 10 ml. After the titanium(IV) and ytterbium(III) had been sorbed onto the resin, the titanium(IV) was eluted with 200 ml. of the alcohol-nitric acid solvent. The ytterbium(III) was then stripped from the column with 100 ml. 0.1M nitric acid. The rare earths were stripped from the column similarly in the other separation experiments. Copper(II), (D = 14), can be separated from 0.1 mmole of ytterbium(III) using a 1.2 x 12 cm. column. A shorter column was used to minimize the volume of eluent needed to elute all the copper(II) from the column.

Because ytterbium(III) has the lowest batch distribution coefficient of the rare earths studied, most of the quantitative separations were carried out using it to represent the rare earths. It was reasoned that ytterbium(III) is the most difficult case, except for lutetium(III), and that any lower rare earth would be separated more easily from other metal ions. Using a 1.2 x 16 cm. column and 1.5M nitric acid in 85% isopropyl alcohol as the eluting medium, quantitative separations of ytterbium(III) from each of the following metal ions were achieved: aluminum(III), cobalt(II), gallium(III), indium(III), iron(III), magnesium(II), manganese(II), nickel(II), vanadium(IV), and zinc(II). A 1.2 x 12 cm. column gave quantitative separations of ytterbium (III) from copper(II), iron(III), and titanium(IV). The amount of ytterbium(III) and the other metal ion in the sample each ranged from 0.05 to 0.25 mmole, with the exception of the titanium(IV) separation mentioned earlier. For separation and analysis of 21 two-component samples (42 individual analyses), the average recovery was 99.9% with a standard deviation of ± 0.3%. These separations are summarized in Table 4.

From the high distribution coefficients of thorium(IV), lead(II), and bismuth(III), it appeared that these metal ions could be separated from some of the rare earths by finding conditions such that the rare earths would be eluted first. It was found that 0.05 mmole of lead(II) and 0.25 mmole of Bi(III) could be separated from 0.25 mmole of samarium(III) by first eluting the samarium(III) with 1.5M nitric acid-55% isopropyl alcohol. Also 0.10 mmole of bismuth(III) was separated from 0.10 mmole of neodymium(III) by eluting neodymium(III) first with 1.5M nitric acid-45% isopropyl alcohol. The average recovery here was 99.9% with a standard deviation of ± 0.25%. The breakthrough and elution volumes of these metals are shown in Table 5 and the separation results in Table 6. The distribution coefficients in Figure 5 indicate that Pb(II) should be easily separated from Nd (III). From Table 5 it can be observed that the Nd(III) tails too much for a quantitative separation from Pb(II) with a 16 cm. column.

Table 4. Metal separations on Amberlyst XN-1002 using 1.5M nitric acid-85% isopropyl alcohol. Column dimensions 1.2 cm. by 16 cm.

Metals separated, mmoles	Eluent (ml. 1.5M HNO_3-85% isopropyl alcohol)	EDTA titrations	
		Theory,ml.	Found,ml.
Al(III) 0.10	145	4.46	4.44[a]
Yb(III) 0.25	---	7.92	7.93
Co(II) 0.25	120	4.77	4.77
Yb(III) 0.25	---	5.01	4.99
Cu(II) 0.10	180(12 cm. column)	9.73	9.69
Yb(III) 0.10	---	8.96	8.93
Fe(III) 0.10	125(12 cm. column)	8.98	8.98
Yb(III) 0.10	---	9.02	8.96
Fe(III) 0.10	150	10.76	10.69
Yb(III) 0.10	---	9.12	9.15
Ga(III) 0.25	145	9.25	9.25
Yb(III) 0.25	---	8.30	8.31
In(III) 0.25	155	8.92	8.92
Yb(III) 0.25	---	8.30	8.32
Mg(II) 0.25	90	8.11	8.14
Yb(III) 0.25	--	8.14	8.14
Mn(II) 0.25	130	8.08	8.06
Yb(III) 0.25		8.30	8.32
Ni(II) 0.25	120	9.24	9.23
Yb(III) 0.25	---	7.98	7.99
Ti(IV) 0.10	200(12 cm. column)	----	----
Yb(III) 0.005	---	0.00500[b]	0.00499[b]
V(IV) 0.20	90	10.75	10.75
Yb(III) 0.25	--	8.04	8.04
Zn(II) 0.25	115	8.70	8.71
Yb(III) 0.25	---	8.04	8.04

[a] All data are given as the average of two determinations.

[b] Mmole Yb(III) determined spectrophotometrically.

Table 5. Breakthrough and elution volumes in 1.5M HNO_3-isopropyl alcohol using a 16 cm. column (Flow rate 0.5 ml./min.)

Metal ion eluted	Eluting solvent	Breakthrough volume, ml.	Elution volume, ml.
0.20 mmole Sm(III)	1.5MHNO_3-55% isopropyl alcohol	0-10	90
0.20 mmole Nd(III)	" "	0-20	190
0.10 mmole Pb(II)	" "	100	---
0.05 mmole Pb(II)	" "	190	---
0.15 mmole Bi(III)	" "	240	---
0.25 mmole Nd(III)	1.5M HNO_3-45% isopropyl alcohol	0-10	100
0.10 mmole Bi(III)	" "	160	---
0.25 mmole Pr(III)	" "	0-10	140

Table 6. Metal separations on Amberlyst XN-1002 using 1.5M nitric acid-isopropyl alcohol. Column dimensions 1.2 cm. by 16 cm.

Metals separated, mmoles	Eluting solvent	EDTA titrations	
		Theory, ml.	Found, ml.
Sm(III) 0.25	110 ml. 1.5M HNO_3-55% isopropyl alcohol	4.93	4.93[a]
Bi(III) 0.25	-----	8.39	8.40
Sm(III) 0.25	100 ml. 1.5M HNO_3-55% isopropyl alcohol	9.08	9.04
Pb(II) 0.05	-----	9.86	9.84
Nd(III) 0.10	125 ml. 1.5M HNO_3-45% isopropyl alcohol	7.78	7.75
Bi(III) 0.10	-----	9.17	9.21

[a] All data are given as the average of two determinations.

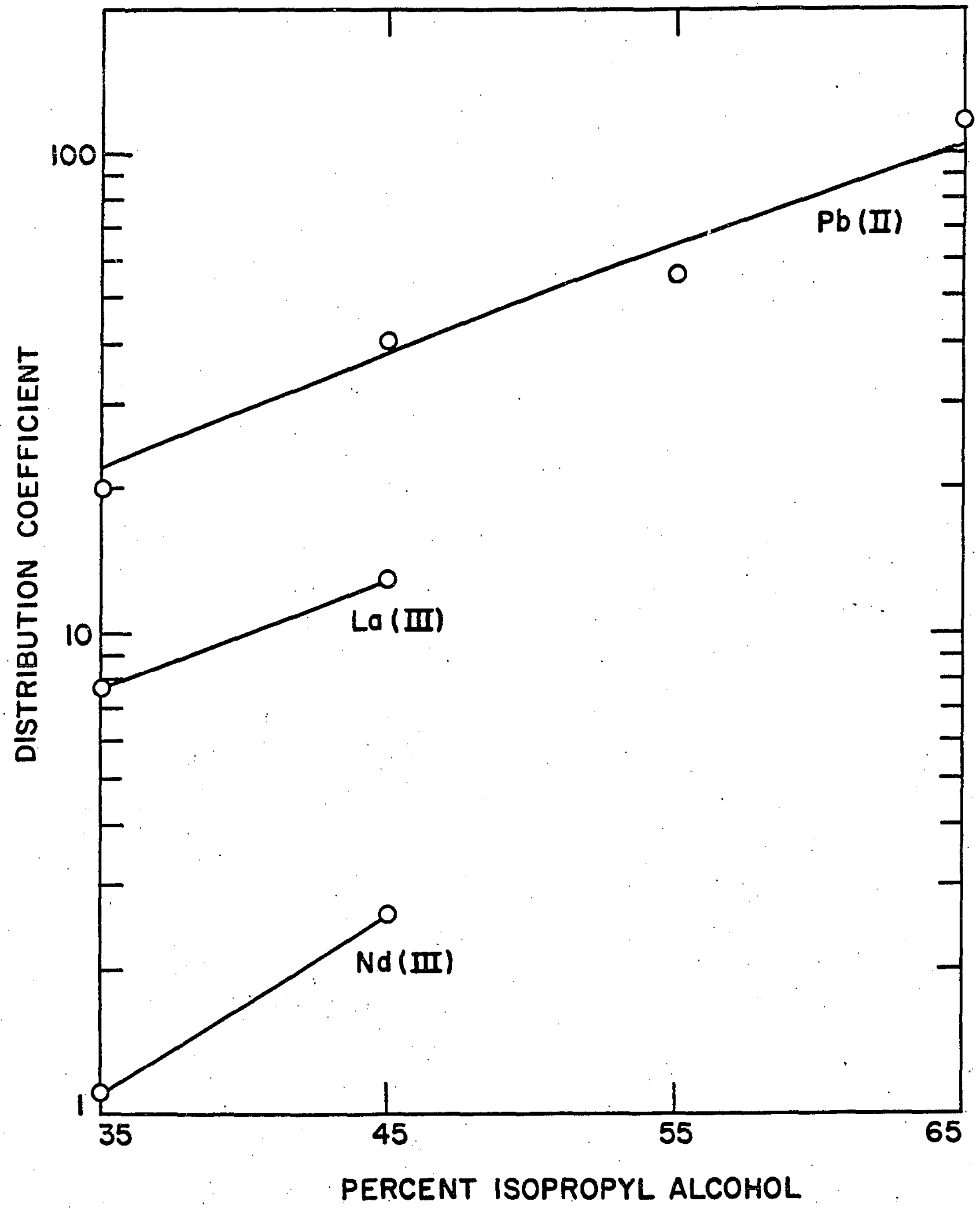


Figure 5. Distribution coefficients of lead(II), lanthanum(III), and neodymium(III) on Amberlyst XN-1002 as a function of isopropyl alcohol concentration at 1.5M nitric acid concentration

When this work was essentially complete, a method of Korkisch and Arrhenius (19) came to our attention. These workers separated rare earths as a group from several other metal ions by anion exchange, using 0.5M nitric acid in a 90% acetic acid-10% aqueous solvent system. While this system works at the very low loadings suggested by Korkisch and Arrhenius, we found that amounts of ytterbium(III) greater than approximately 10 mg. break through too soon to permit a quantitative column separation. Comparison of the acetic acid and the isopropyl alcohol system proposed in this thesis shows that 1 mg. (0.0057 mmole) portions of ytterbium(III) break through considerably sooner with the acetic acid system than with the isopropyl alcohol system, while a typical bivalent metal, cobalt(II), is completely eluted in about the same volume in the two systems (Table 7). Our experiments also show that the nitric acid-methanol system, recommended earlier for separation of rare earths from other metal ions, is limited to very small amounts when the heavier rare earths are used.

Table 7. Comparison of isopropyl alcohol-nitric acid-Amberlyst system with acetic acid-nitric acid-Dowex system (Flow rate 0.5 ml./min. 15 cm. column)

Metal ion eluted	Elution conditions	Breakthrough volume, ml.	Elution volume, ml.
0.25 mmole Co(II)	1.5M HNO_3-85% isopropyl alcohol, Amberlyst column	---	100
	0.5M HNO_3-90% acetic acid, Dowex column	---	90
0.0057 mmole Yb(III)	1.5M HNO_3-85% isopropyl alcohol, Amberlyst column	350	---
	0.5M HNO_3-90% acetic acid, Dowex column	210	---

SEPARATION OF THE RARE EARTHS FROM EACH OTHER

Survey of the Literature

Most ion exchange separations of the rare earths are carried out by cation exchange techniques. An extensive review of these methods has been given by Powell (22, p. 55).

Anion exchange had been used very little because of the small tendency for the rare earths to form complexes with simple inorganic ions. Of the inorganic ligands, nitrate has been used most often in the past few years because of its relatively greater complexing strength with the rare earths.

Marcus and Nelson (23) used 3 to 4M lithium nitrate in dilute nitric acid to separate adjoining rare earths from lanthanum(III) to europium(III) with a separation factor of 1.4. The separation factor for europium and terbium and for terbium and ytherbium was only 1.5.

Marcus and Abrahamer (24) also determined the distribution coefficients of the rare earths in up to 10M lithium nitrate solutions.

Faris and Warton (17), using nitric acid in methanol, obtained some interesting separation factors for various rare earths. Some of their separation factors were comparable and some better than the 0.3M isobutyrate cation-exchange resin system, which is one of the popular separation methods.

Edge (25) also used nitric acid in methanol. He was able to find conditions at which the elements lanthanum through neodymium could be readily separated from the rare earths samarium through lutetium.

Edge (26) determined the distribution coefficients of yttrium(III), neodymium(III), and lanthanum(III) in nitric acid-ethyl alcohol solvents. He found that the best separation factors occurred at higher alcohol percentages.

Edge (27,28) also determined the distribution coefficients of yttrium(III), neodymium(III), and lanthanum(III) in hydrochloric acid-ethyl alcohol solvent, and also of these metals plus praseodymium(III) in sulfuric acid-ethyl alcohol solvent. In hydrochloric acid these metals were not resolvable. In sulfuric acid the separation factors were better but still did not appear to be as good as in nitric acid.

Results and Discussion

Authors mentioned earlier (23,24) have determined that aqueous lithium nitrate solutions give better separation factors with the rare earths than nitric acid. They felt that the success of their methods was due to the stripping away of the hydration shell of the rare earths with lithium(I). Lithium(I), being an ion with a high charge to radius ratio, solvates water molecules very effectively. Any stripping away of water molecules then would allow stronger interactions between the metal ion and the ligand. The interactions could be of the electrostatic or of the covalent bonding type or a combination of the two.

The work of Maeck et al. (29) showed that this type of reasoning might be valid. They studied the absorption bands of intra 4f electron transitions in the rare earths. The effect of complexing ligands is normally slight on these transitions because of the shielding by the 5s and 5p electrons. However, when the rare earths were extracted into a low solvating medium such as tetrabutylammonium nitrate, wavelength shifts and intensity changes were observed. This can be credited to the removal of the shielding waters of hydrations from the rare earths which allow the ligands to approach closer to the bare metal ion.

Following this line of thinking, the work in this thesis on the separation of rare earths from each other was started. It was felt that using an organic solvent, less solvating than water, in combination with lithium nitrate would allow greater complexation to take place. Also it was felt that the removal of water of hydration from the rare earths would tend to accentuate size differences between individual members of the series.

The organic solvents chosen for study with lithium nitrate were acetone, methanol and isopropyl alcohol. In 90% isopropyl alcohol the distribution coefficients of gadolinium(III) and ytterbium(III) increased in a regular fashion. As can be seen from Figure 6 and Table 8, the distribution coefficients of gadolinium(III) increase faster than those of ytterbium(III). Thus the separation factor for these

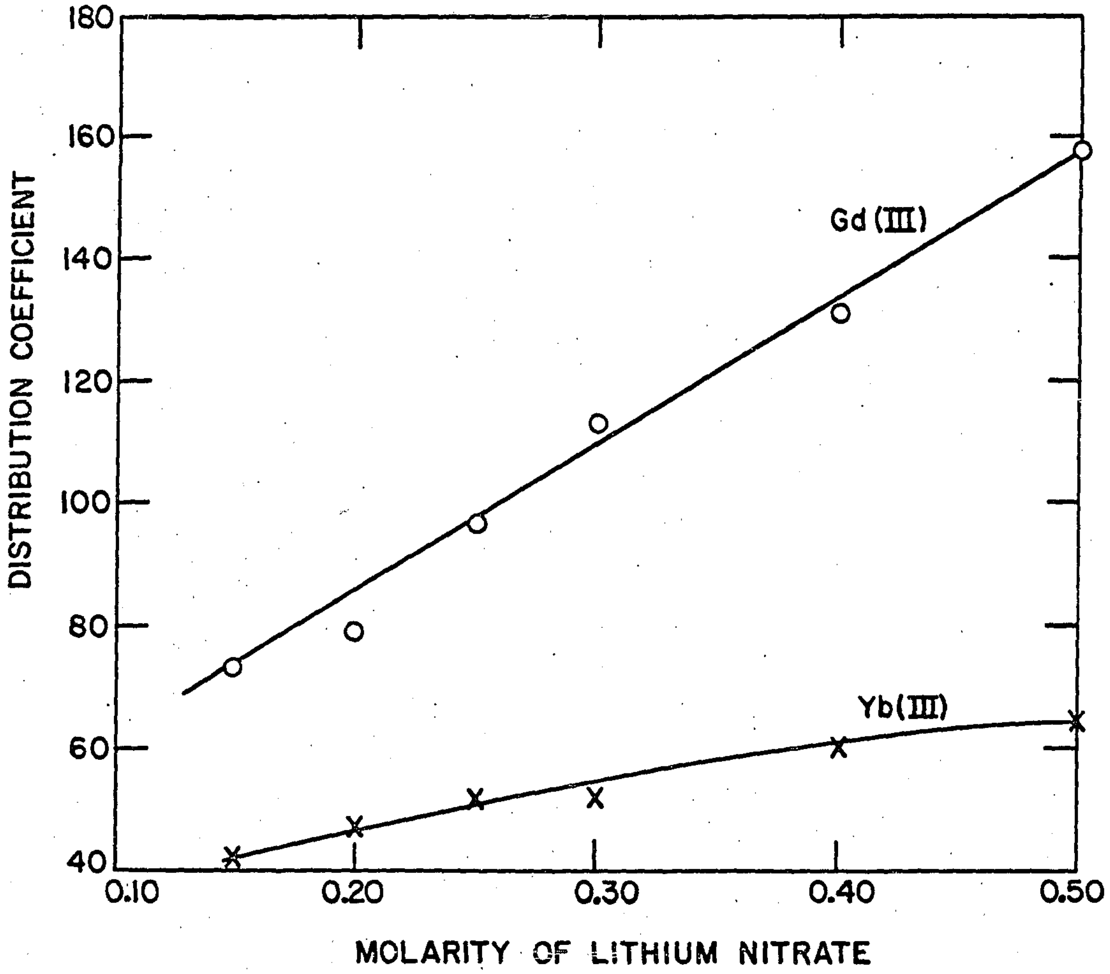


Figure 6. Distribution coefficients of ytterbium(III) and gadolinium(III) in a solution of 90% isopropyl alcohol-0.005M nitric acid as a function of lithium nitrate concentration

elements can be improved by the addition of more lithium nitrate. Unfortunately, good separation factors could not be obtained because of the limited solubility of lithium nitrate in isopropyl alcohol.

Table 8. Distribution coefficients of ytterbium(III) and gadolinium(III) in 90% organic solvent-0.005M nitric acid with varying lithium nitrate concentration

$LiNO_3$	Metal ion		Separation factor
	Yb(III)	Gd(III)	
	Acetone		
0.10	11.7	13.2	1.1
0.30	11.0	12.3	1.1
0.50	10.2	----	---
0.70	----	9.2	---
	Isopropyl alcohol		
0.15	41.6	72.3	1.7
0.20	46.6	79.0	1.7
0.25	52.7	97.0	1.8
0.30	52.0	113	2.2
0.40	59.4	131	2.2
0.50	63.7	158	2.5

In 90% acetone the distribution coefficients of the rare earths decrease with an increase in lithium nitrate concentration as seen in Figure 7 and Table 8. The reason for this decrease is not immediately clear. It is clear though that the separation factors are too poor in this solvent for it to be used in separating the rare earths from each other.

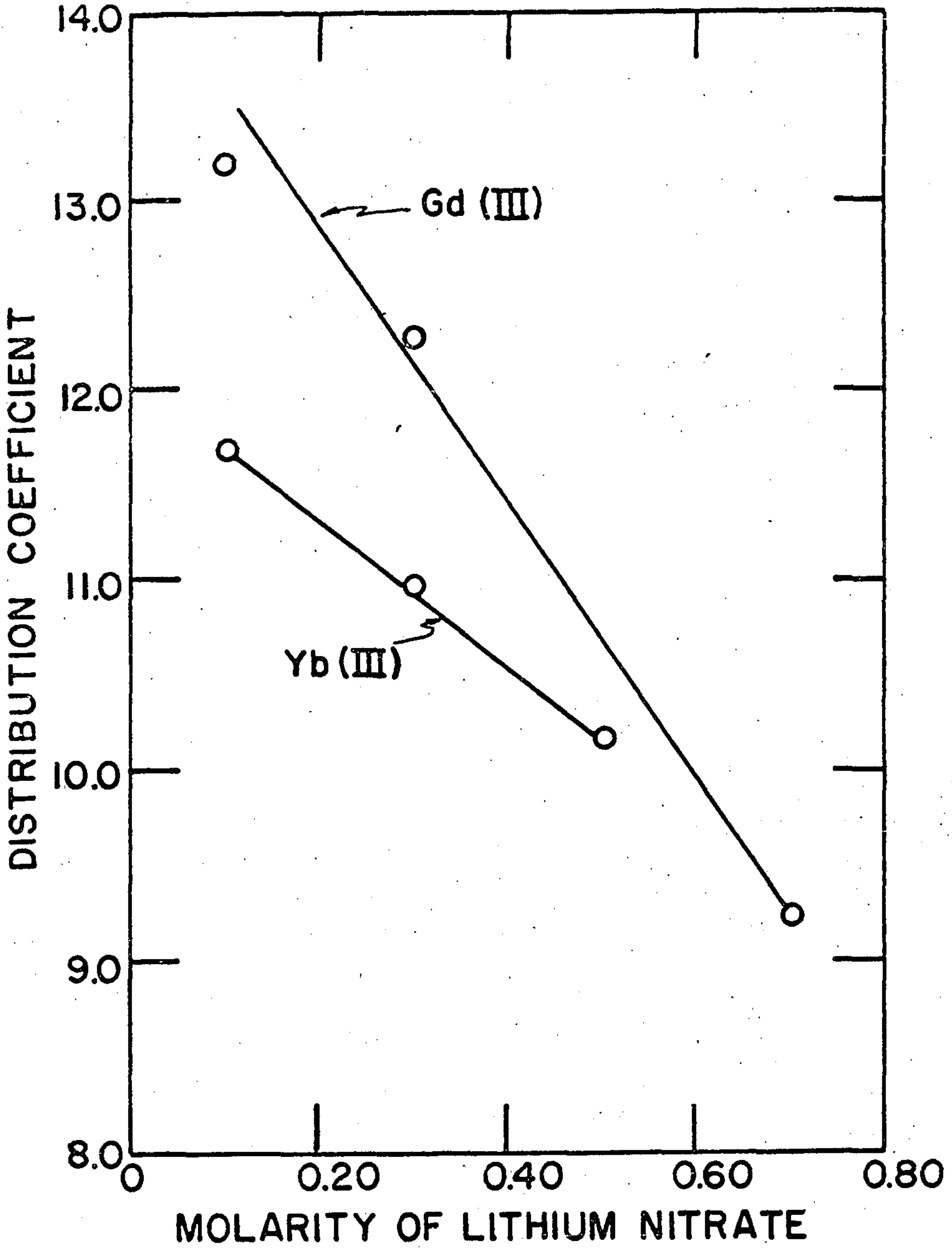


Figure 7. Distribution coefficients of gadolinium(III) and ytterbium(III) in a solution of 90% acetone-0.006M nitric acid as a function of lithium nitrate concentration

In 95% methanol the distribution coefficients (see Figure 8 and Table 9) increase regularly as in 90% isopropyl alcohol. A comparison of the separation factors at any particular concentration of lithium nitrate in 95% methanol and 90% isopropyl alcohol, for the two rare earths studied, shows that isopropyl alcohol would be the better separation medium. This is negated by the fact that lithium nitrate is more soluble in methanol and thus allows the separation factor to be increased more by the further addition of this salt. Unfortunately, the solubility limit of lithium nitrate in methanol is reached before a really good separation factor can be obtained.

Table 9. Distribution coefficients of ytterbium(III) and gadolinium(III) in 95% methyl alcohol-0.005M nitric acid with varying lithium nitrate concentration

$LiNO_3$	Metal ion		Separation factor
	Yb(III)	Gd(III)	
0.10	24	23	1.0
0.30	--	32	---
0.50	30	44	1.5
0.70	34	52	1.5
0.90	--	60	---
1.10	--	69	---
1.30	--	76	---
1.50	--	86	---
2.00	46	104	2.3
2.50	49.5	116	2.3
3.00	50	121	2.4
3.25	51.5	129	2.5

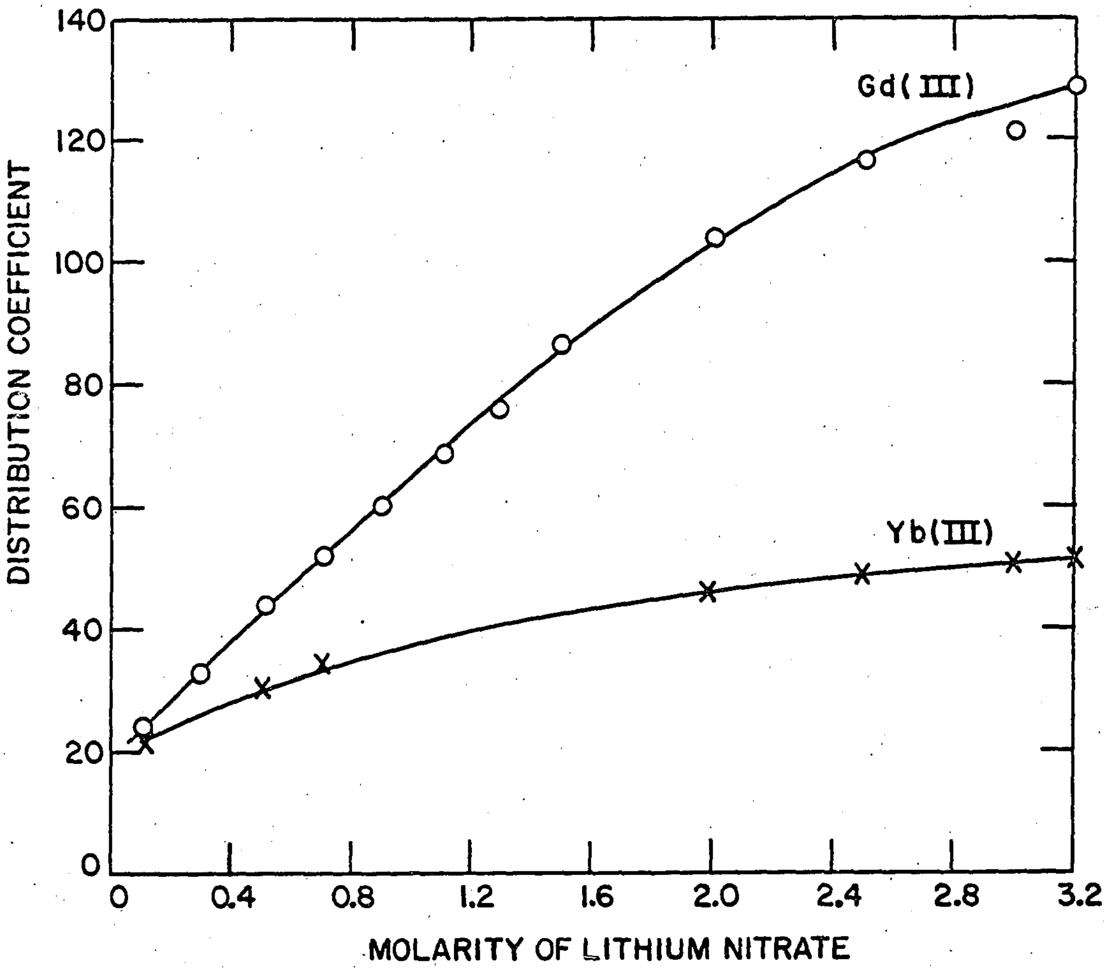


Figure 8. Distribution coefficients of ytterbium(III) and gadolinium(III) in a solution of 95% methyl alcohol-0.005M nitric acid as a function of lithium nitrate concentration

Since the concentration of nitrate can not be increased far enough by the addition of lithium nitrate, it was hoped that the addition of nitric acid to the lithium nitrate-methanol solvent mixture might further increase the separation factors. The result of adding nitric acid was to decrease the distribution coefficients of various rare earths at different rates. Owing to the different rates of decrease, the separation factors increased. The distribution coefficients dropped sharply at first and then at a moderately slow rate as shown in Figures 9-11 and Tables 10-12. The decrease can perhaps be attributed to a reaction of the type

$$\mathrm{Yb(NO_3^-)_4^-}_{(r)} + \mathrm{HNO_3}_{(r)} = \mathrm{HYb(NO_3^-)_4}_{(r)} + \mathrm{NO_3^-}_{(r)} \qquad (6)$$

taking place in the resin phase. The neutral species formed would then distribute themselves between the solution and resin phases. This reaction would take place in the resin phase in preference to the solution phase because of the lower dielectric constant of the resin phase, which favors the formation of undissociated species. Using data taken from invasion experiments (Figure 16), crude calculations show that enough hydrogen ions invade the resin to be available for the above reaction to take place. Horne (30) has also mentioned the possibility of acidic species being formed in the resin phase.

Using Figure 11 and Table 12, calculations can be made showing that the separation factors for different rare earths

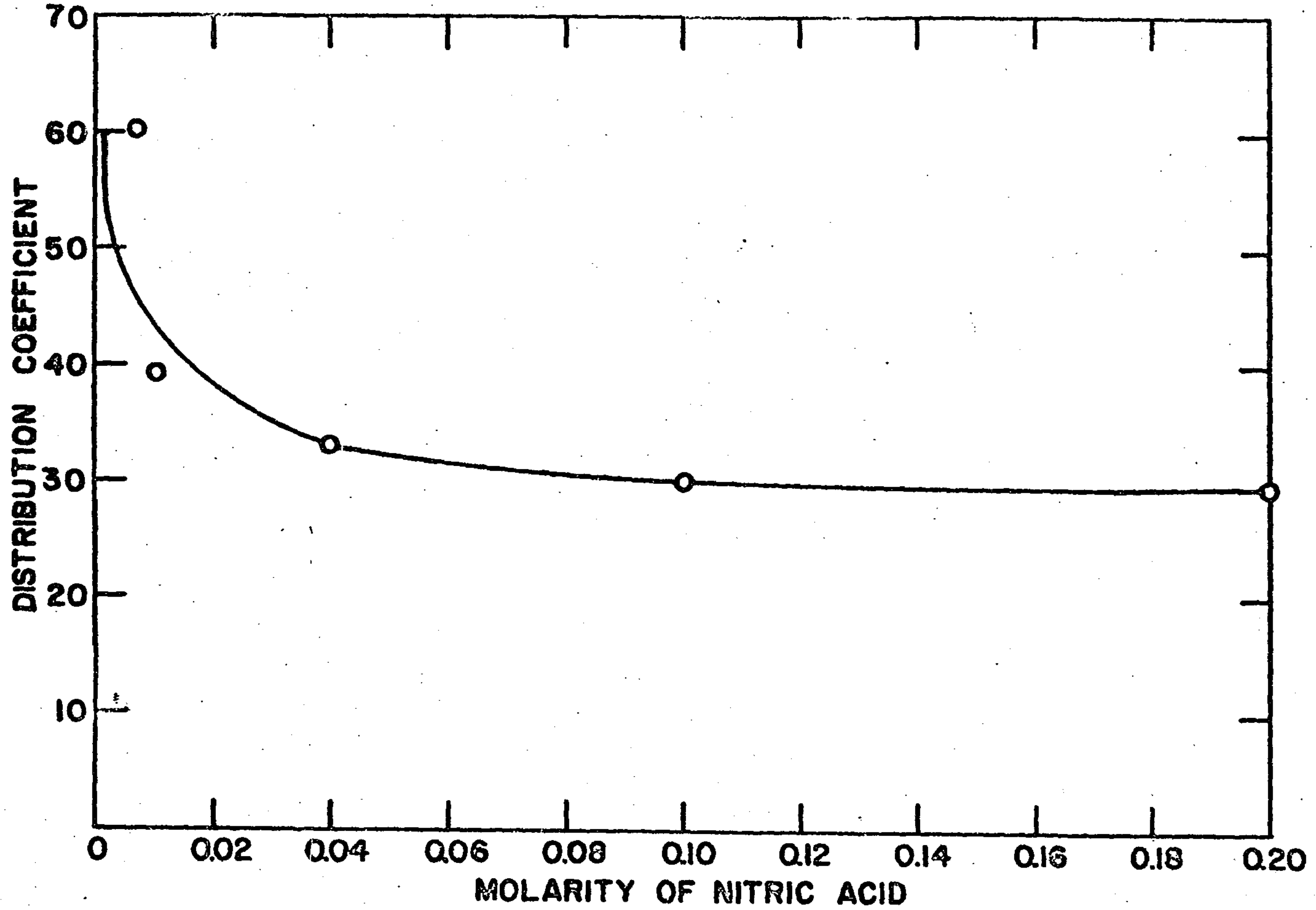
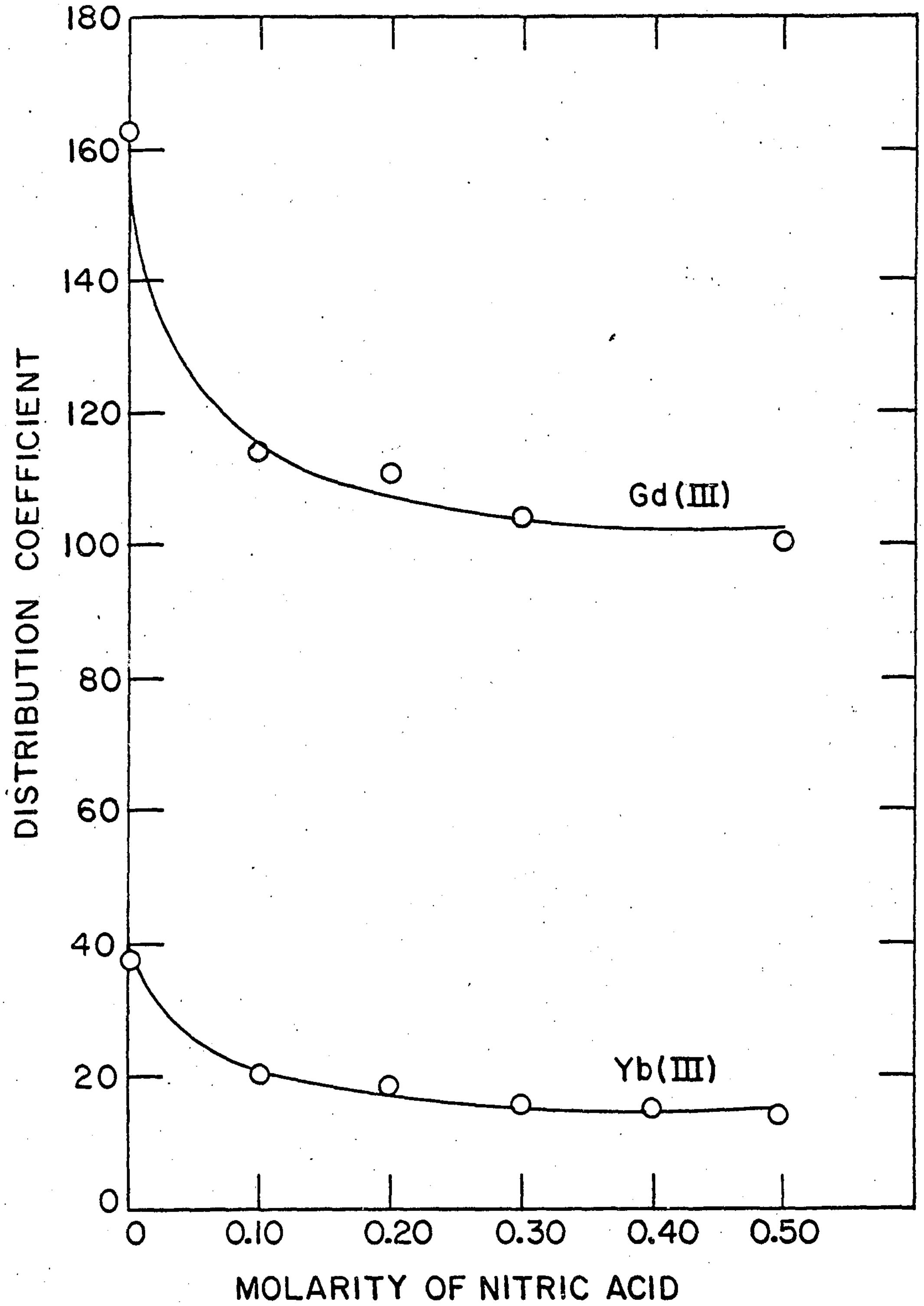


Figure 9. Distribution coefficients of holmium(III) in a solution of 92.5% methanol-3.00M lithium nitrate as a function of nitric acid concentration

Figure 10. Distribution coefficients of gadolinium(III) and ytterbium(III) in a solution of 95% methanol-3.00M lithium nitrate as a function of nitric acid concentration


DISTRIBUTION COEFFICIENT
180
160
140
120
100
80
60
40
20
0
0
0.10
0.20
0.30
0.40
0.50
MOLARITY OF NITRIC ACID
Gd(III)
Yb(III)

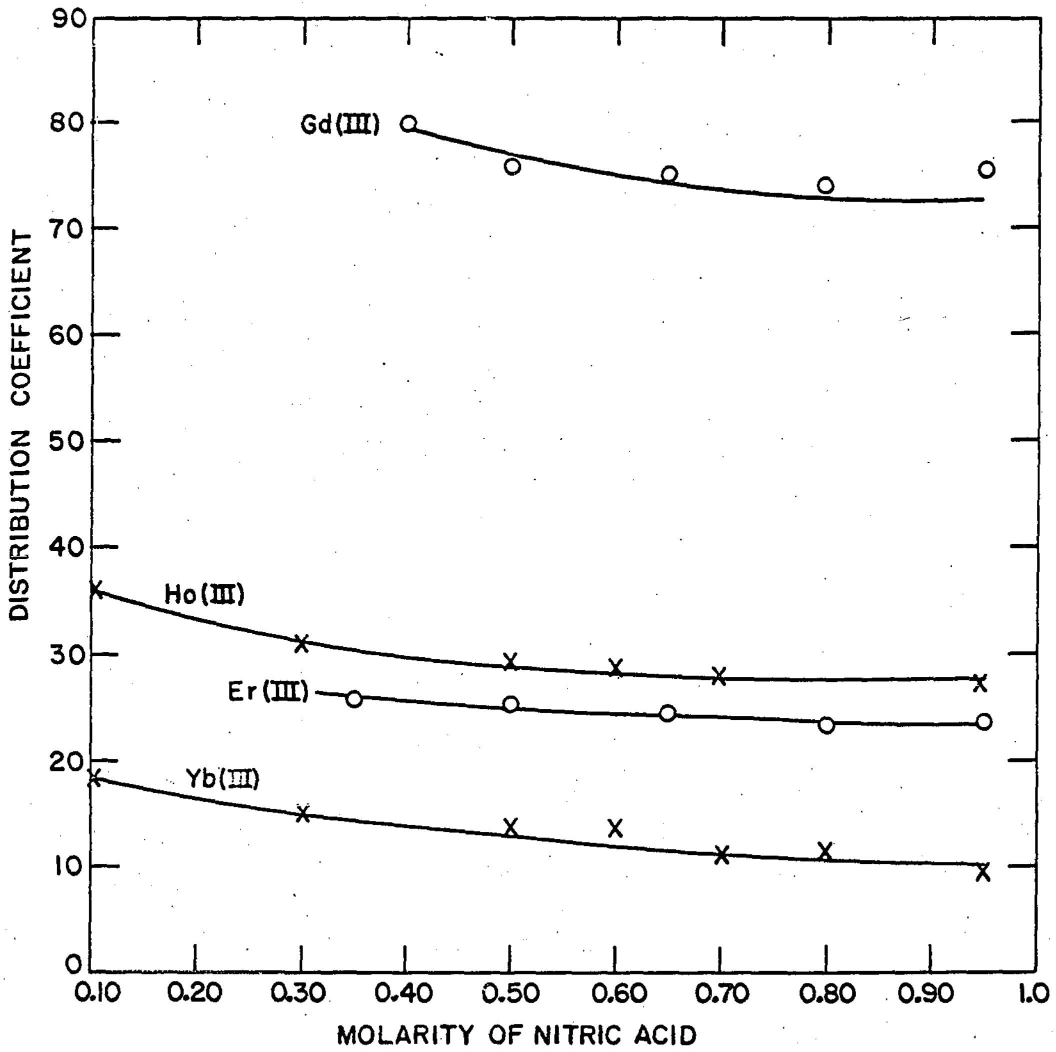


Figure 11. Distribution coefficients in a solution of 92.5% methanol-3.00M lithium nitrate as a function of nitric acid concentration

increase slowly as nitric acid is added. It is felt that no more than about 0.95M nitric acid should be used in order to avoid the instability associated with highly acidic alcoholic solutions.

Table 10. Distribution coefficients of holmium(III) in 92.5% methanol-3.00M lithium nitrate with varying nitric acid concentration

HNO_3	Distribution coefficient
0.006	60.5
0.01	39.0
0.04	33.0
0.10	30.0
0.20	29.5

Table 11. Distribution coefficients of gadolinium(III) and ytterbium(III) in 95% methanol-3.00M lithium nitrate with varying nitric acid concentration

HNO_3	Metal ion		α^{Gd}_{Yb}
	Yb(III)	Gd(III)	
0.003	37.5	163	4.35
0.10	20.5	114	5.55
0.20	18.5	111	6.00
0.30	16.5	104	6.25
0.40	16.0	---	----
0.50	14.5	99.5	6.85

Table 12. Distribution coefficients of rare earths in 92.5% methanol-3.00M lithium nitrate with varying nitric acid concentration

HNO_3	Metal ion			
	Yb(III)	Er(III)	Ho(III)	Gd(III)
0.10	18.0	----	36.0	----
0.30	15.0	----	31.0	----
0.35	----	25.5	----	80.0
0.50	13.5	25.0	29.5	76.0
0.60	13.0	----	28.5	----
0.65	----	24.5	----	75.0
0.70	11.0	----	28.0	----
0.80	11.5	23.5	----	74.0
0.95	9.5	23.5	27.5	75.0

Calculations can also be made from Figure 12 and Table 13 showing that the separation factor does not change significantly from 85% to 95% methanol using a fairly concentrated lithium nitrate-nitric acid mixture.

Table 13. Distribution coefficients of holmium(III) and ytterbium(III) in 3.50M lithium nitrate-0.55M nitric acid with varying percentages of methyl alcohol

% methanol	Metal ion		α^{Ho}_{Yb}
	Yb(III)	Ho(III)	
85	----	18	---
90	10.4	25.3	2.5
92.5	12.1	28.6	2.4
95	15.1	35.6	2.4

To determine if the system performed ideally, column experiments were carried out using two different solvent mixtures. From Figure 13 and Figure 14 it was found, with the aid of Equation 3, that the elution characteristics were close to ideality.

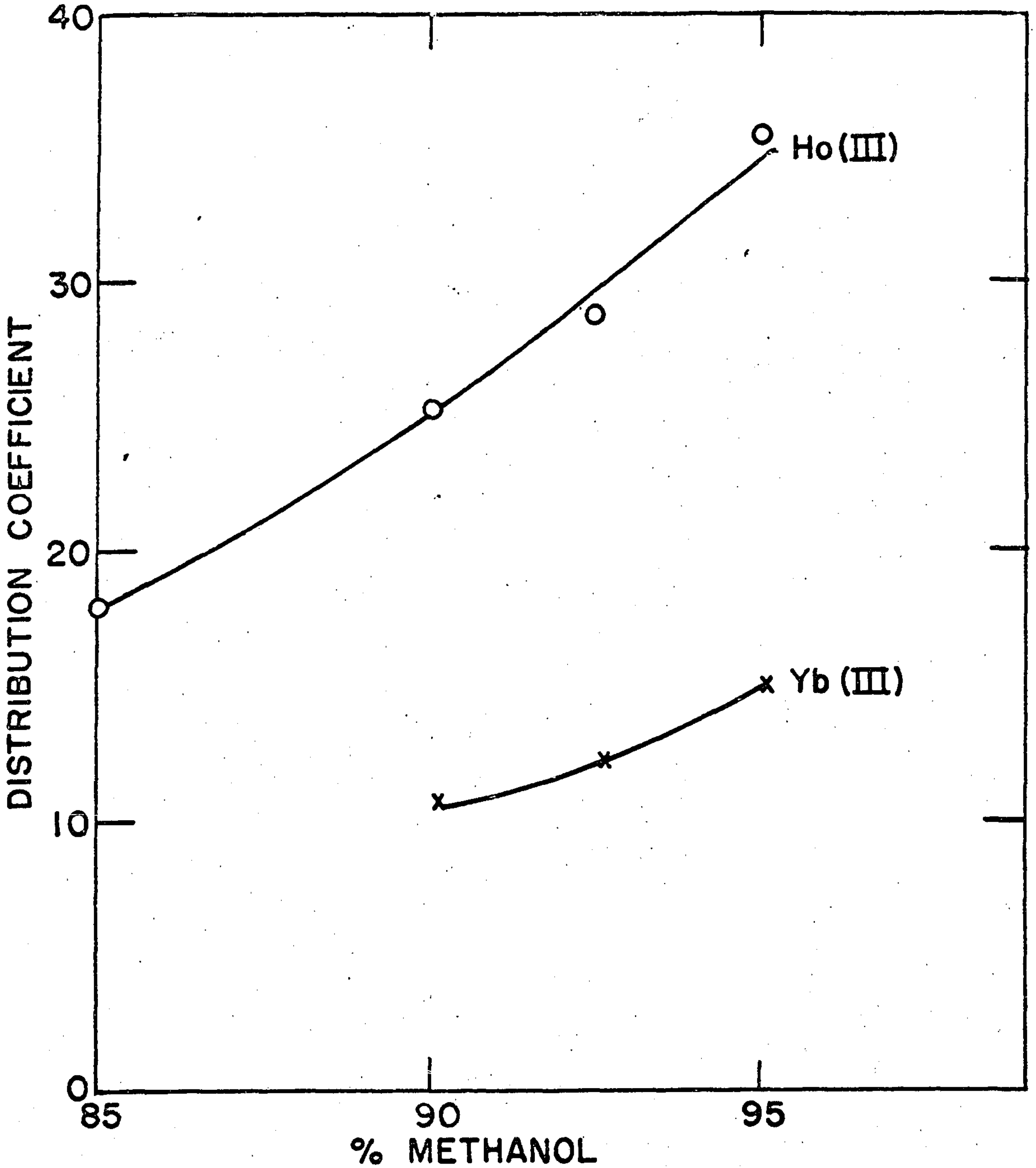
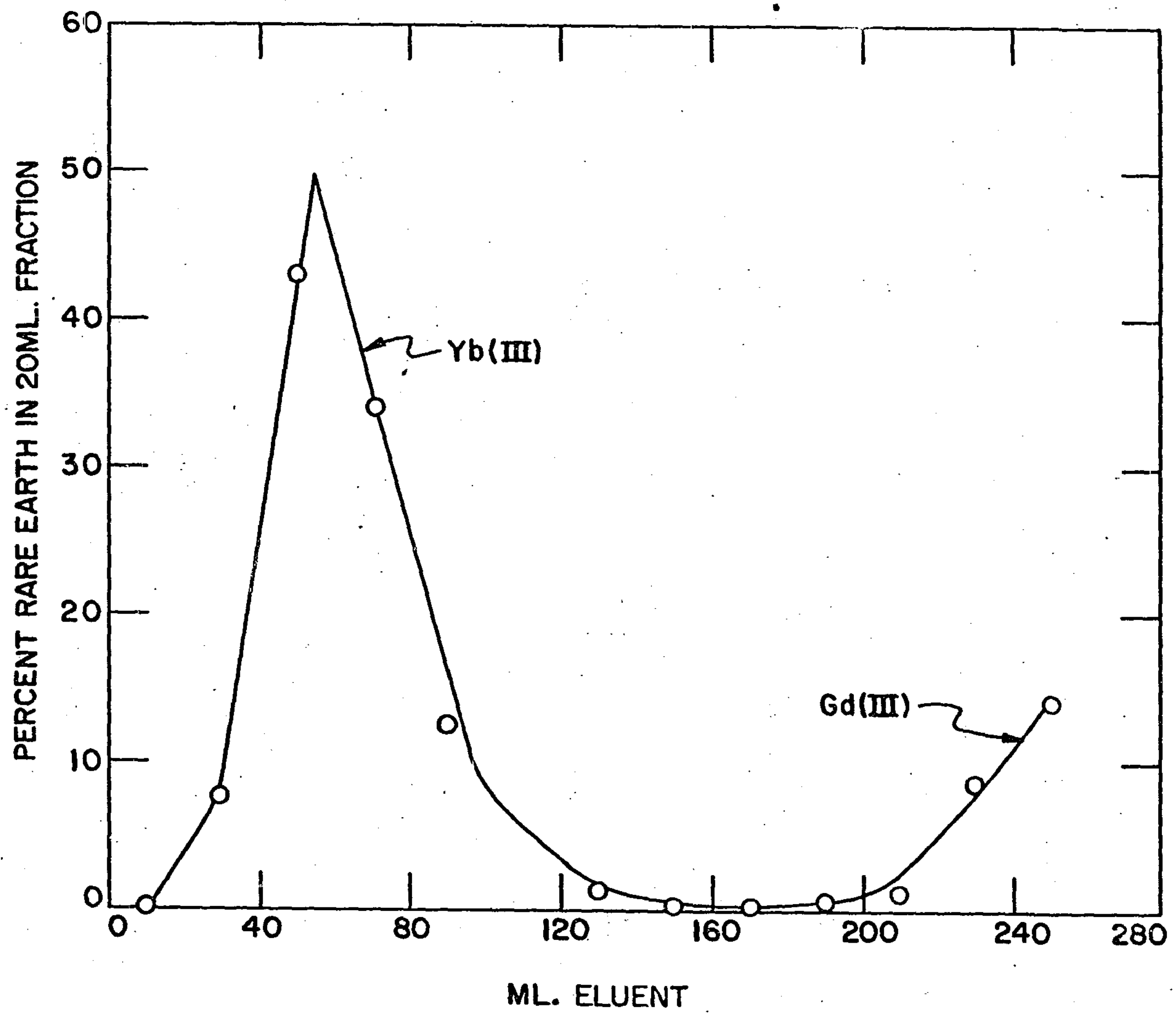


Figure 12. Distribution coefficients of holmium(III) and ytterbium(III) in a solution of 3.50M lithium nitrate-0.55M nitric acid as a function of percentage methanol

Figure 13. Elution of 0.10 mmole ytterbium(III) and 0.005 mmole gadolinium(III) with a solution of 92.5% methanol-3.00M lithium nitrate-0.30M nitric acid on separate 12 cm. columns of Amberlyst XN-1002 resin. Flow rate was 0.25-0.30 ml./min.


PERCENT RARE EARTH IN 20ML. FRACTION
60
50
40
30
20
10
0
0
40
80
120
160
200
240
280
ML. ELUENT
Yb(III)
Gd(III)

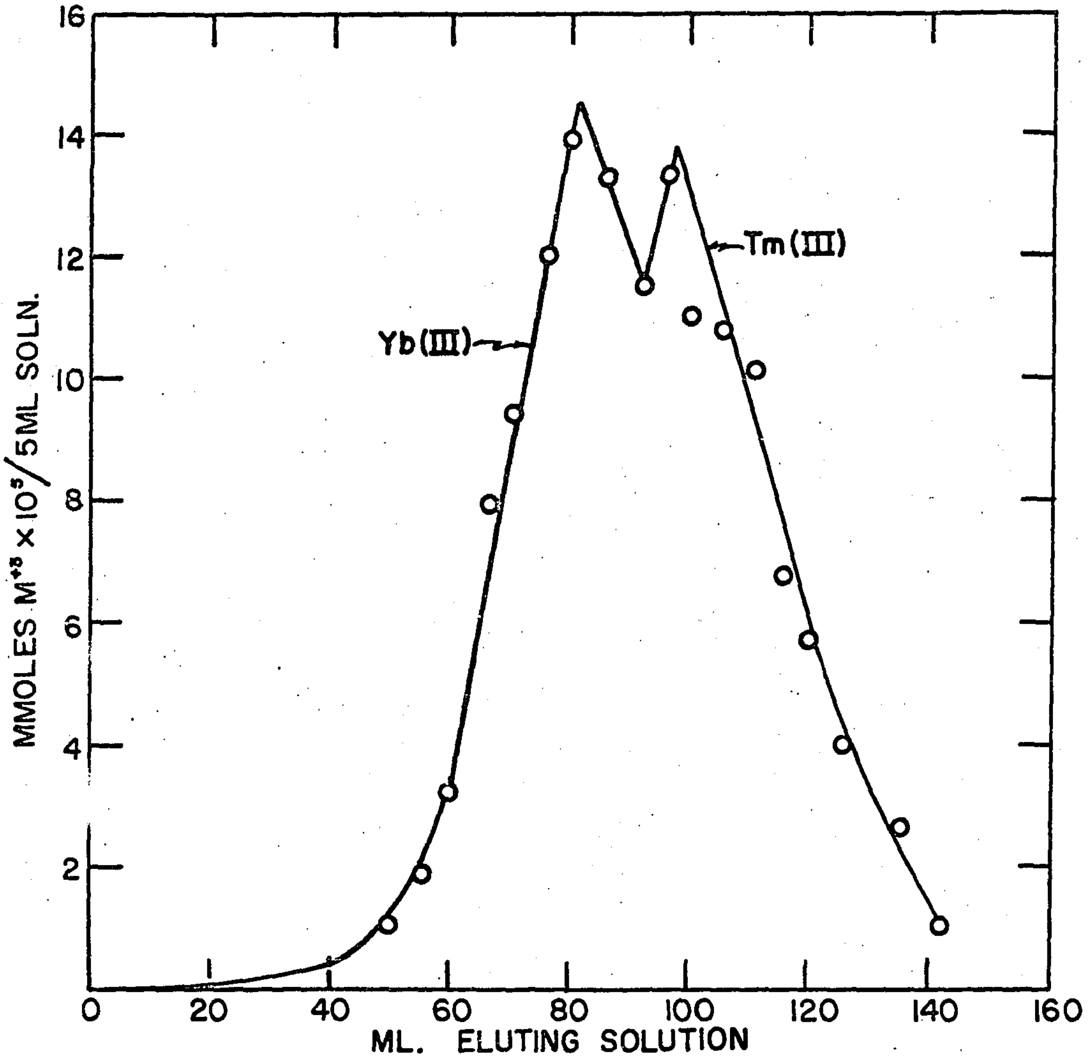


Figure 14. Elution of ytterbium(III) and thulium(III) with a solution of 92.5% methanol-3.00M lithium nitrate-0.95M nitric acid from a 50 cm. column of Amberlyst XN-1002 resin. Flow rate was 0.10-0.20 ml./min.

In order to compare this system with others, distribution coefficients of the rare earths were determined in a solvent mixture of 92.5% methanol-3.00M lithium nitrate-0.95M nitric acid. They change in a regular manner from ytterbium(III) to lanthanum(III) as seen in Figure 15 and Table 14. Table 15 compares the separation factors of adjacent rare earths for this solvent system with some of the other well-known systems. It can be seen that the separation factors in the methanol-lithium nitrate-nitric acid system are comparable in many cases, and better in some, to those shown from the other mediums.

Table 14. Distribution coefficients of rare earths in 92.5% methanol-3.00M lithium nitrate-0.95M nitric acid

Rare earth(III)	Distribution coefficient
Yb	9.95
Tm	15.3
Er	22.5
Ho	27.5
Dy	36.6
Tb	47.6
Gd	73
Eu	128
Sm	237
Nd	721
Pr	954
Ce	1060
La	1130
Y	21.6

It is felt that this system has some advantages over those using organic acids. In separations with organic acids, such as EDTA, the acid has to be destroyed before an

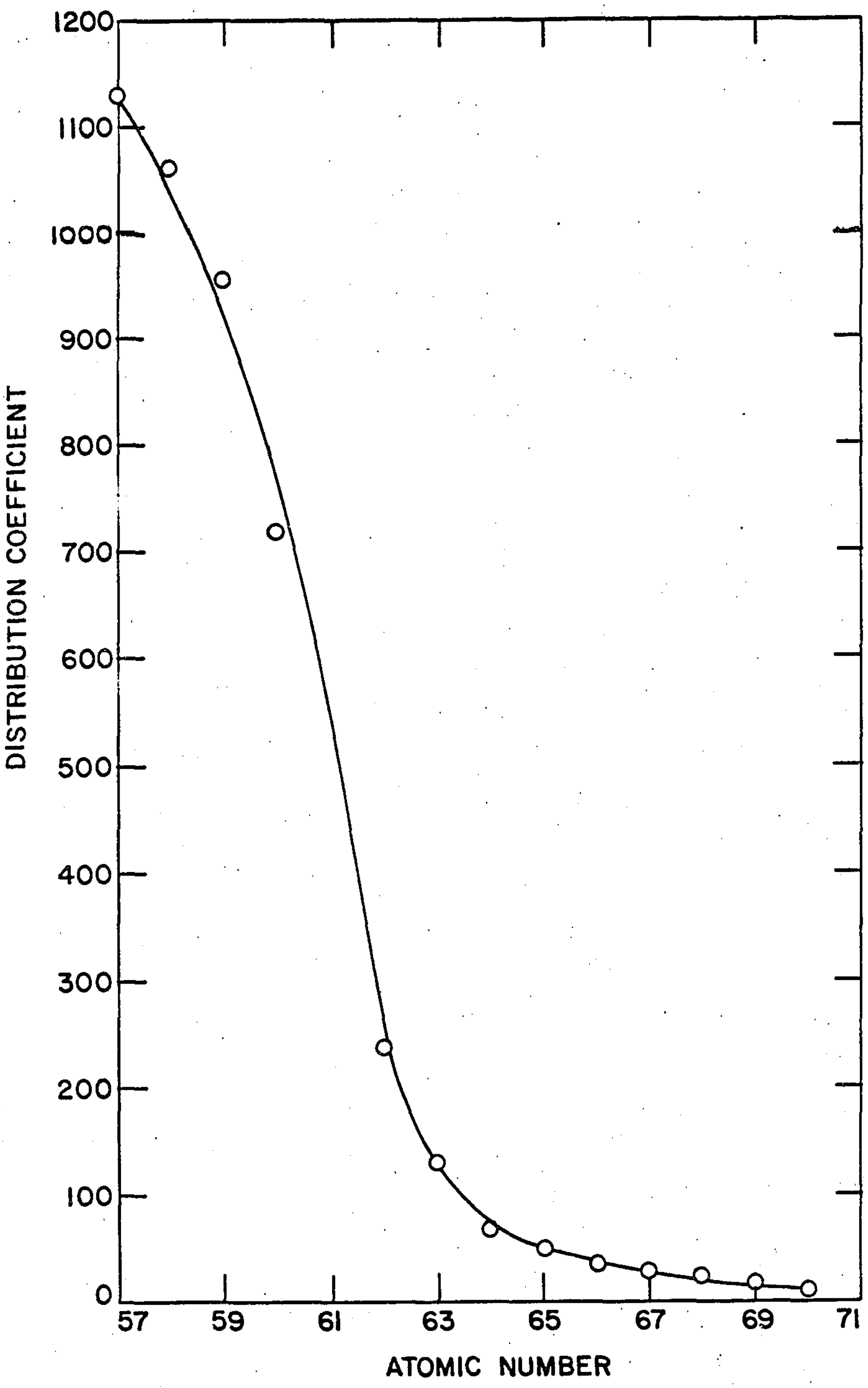


Figure 15. Distribution coefficients of the rare earths in a solution of 92.5% methanol-3.00M lithium nitrate-0.95M nitric acid

analysis can be performed.' This is a step most analytical chemists would rather avoid. In the proposed system the rare earths can be determined directly after elution from the column or at most after simple evaporation of the methanol. If it is necessary to obtain a pure rare earth solution after the separation, it is felt that this would be easiest to accomplish with the proposed system. It also has an advantage over the methanol-nitric acid system, in that, in the methanol-nitric acid solvent the best separation factors occur under the conditions where the distribution coefficients are comparatively high. This necessitates using larger volumes of eluent with longer elution times than would be needed in the proposed system.

Table 15. Separation factors of adjacent rare earths in different solvent systems

Rare earths (III)	Solvent			
	EDTA catex resin	HEDTA catex resin	1.57M HNO_3 90% methanol	3.00M $LiNO_3$ 0.95M HNO_3 92.5% methanol
Yb-Tm	1.8	1.6	1.12	1.54
Tm-Er	---	2.0	1.15	1.47
Er-Ho	1.8	1.2	1.22	1.22
Ho-Dy	2.6	ca 1.0	1.21	1.40
Dy-Tb	2.3	ca 1.0	1.48	1.30
Tb-Gd	4.2	ca 1.0	1.47	1.52
Gd-Eu	1.05	ca 0.7	1.95	1.76
Eu-Sm	1.5	ca 1.0	2.10	1.85
Sm-Nd	3.2	2.6	6.50	3.05
Nd-Pr	---	1.8	2.26	1.32
Pr-Ce	---	2.8	1.80	1.11
Ce-La	3.7	5.0	1.75	1.07
Dy-Y	1.6	---	1.59	1.70
Y-Tb	1.5	---	2.82	2.20

ION EXCHANGE THEORY

Invasion Experiments

If anion-exchange resin in the nitrate form is put into a dilute solution of nitric acid, there will be a large concentration difference between the resulting two phases. The nitrate concentration in the resin phase will be larger than the nitrate concentration in the solution phase, and the hydrogen ion concentration in the solution phase will be larger than the hydrogen ion concentration in the resin phase. To attempt to level out these concentration differences, nitrate ions will diffuse into the solution and hydrogen ions will diffuse into the resin. This will disturb the electricial neutrality of the solution and resin and give rise to an electrical potential difference between the two phases. In anion exchangers this so-called "Donnan potential" results in anions being pulled back into the (positively charged) resin phase and cations being pulled back into the (negatively charged) solution. A general equation for the Donnan potential, as given by Helfferich (31), is

$$E_{Don} = \frac{1}{Z_i F} \left(RT \ln \frac{a_i}{\bar{a}_i} - \Pi V_i\right) \qquad (7)$$

E_{Don} is the Donnan potential; Z_i, the ionic charge of the species i (negative for anions); F, the Faraday constant; a_i, the activity of species i in solution; $\bar{a}_i$, the activity of species i in the resin phase; Π, the swelling pressure;

and V_i, the partial molar volume of species i. In this equation changes in the swelling pressure and the molar volume do not normally cause the Donnan potential to change significantly.

It can be seen from Equation 7 that as the activities of the species in the resin and solution phases approach each other the Donnan potential approaches zero. The result is "invasion", i.e., the ion exchanger sorbs significant amounts of electrolyte. The closer the Donnan potential approaches to zero, the higher is invasion.

In nonaqueous solvents more attention must be given to invasion because its magnitude can be much larger than at the same electrolyte concentration in water. When invasion is large, ion-exchange characteristics can be quite radically effected. One main reason for this may be the further complexations that metal complexes undergo in the resin phase when the concentration of ligand is increased.

Using the Donnan potential concept, a possible explanation for the increase of solute invasion with an increase in the mole fraction of isopropyl alcohol in solution, as seen in Figure 16 and Table 16, may be made. The activity of the solute in the solution phase is lowered by a decrease in the dielectric constant of the solvent. This is also true for the solute in the resin phase. In the solution phase the dielectric must be lowered considerably from that of pure water in order to cause a significant degree of association

Figure 16. Sorption of electrolyte into Dowex 1-X8, 20-50 mesh resin as a function of mole fraction isopropyl alcohol

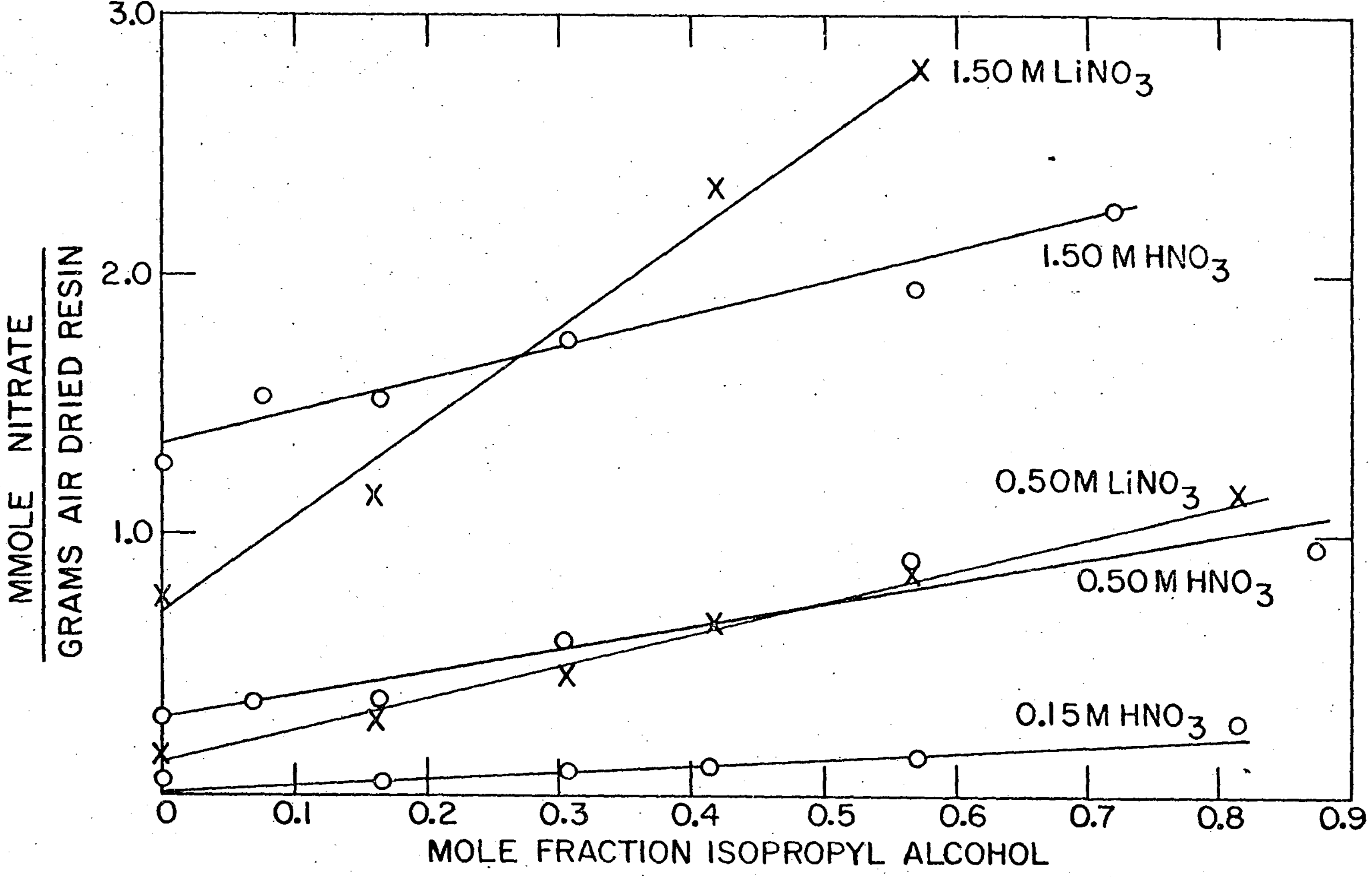

3.0
2.0
1.0
0
MMOLE NITRATE / GRAMS AIR DRIED RESIN
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
MOLE FRACTION ISOPROPYL ALCOHOL
1.50 M LiNO$_3$
1.50 M HNO$_3$
0.50M LiNO$_3$
0.50 M HNO$_3$
0.15 M HNO$_3$

Table 16. Sorption of electrolyte into Dowex 1-X8, 20-50 mesh resin as a function of mole fraction isopropyl alcohol

Mole fraction alcohol	$\frac{\text{Mmole nitrate}}{\text{grams air dried resin}}$				
	0.15M HNO_3	0.50M HNO_3	0.50M $LiNO_3$	1.50M HNO_3	1.50M $LiNO_3$
0	0.050	0.30	0.163	1.27	0.73
0.074	-----	0.35	-----	1.52	----
0.164	0.066	0.36	0.254	1.52	1.16
0.304	0.074	0.59	0.462	1.74	1.74
0.413	0.093	----	0.643	----	2.32
0.570	0.165	0.89	0.860	1.95	2.76
0.72	-----	----	----	2.25	----
0.817	0.256	----	1.16	----	----
0.875	----	0.95	----	----	----

of strong electrolytes. On the other hand, association in the resin phase is significant because of the low dielectric of the resin matrix and a further lowering of the dielectric constant of the resin phase would result in a considerable increase in ion-pair formation. The addition of an organic solvent and its subsequent lowering of the dielectric of both phases, thus, leads to an enhancement of association in the resin phase compared to the solution phase. The difference between the solute activities in the two phases is correspondingly reduced, which leads to the observed increase of invasion as predicted from Equation 7.

Another contributing factor to the increase of invasion may be the increasing amount of neutral species being formed at high concentration of organic solvent. Since the Donnan potential only influences ions and has no effect on neutral species, it follows that invasion will increase as the formation of neutral species increases.

Another factor that may be important in determining the extent of invasion is the solubility of the solute in the solution being equilibrated with the resin. Lithium nitrate is much more soluble in water than in isopropyl alcohol. Thus since the resin phase contains a greater concentration of water (31, p. 512) than the solution phase, the lithium nitrate may partly be just distributing itself on the basis of solubility. This argument is supported by the results of the experiments shown in Figure 17 and Table 17. Considering

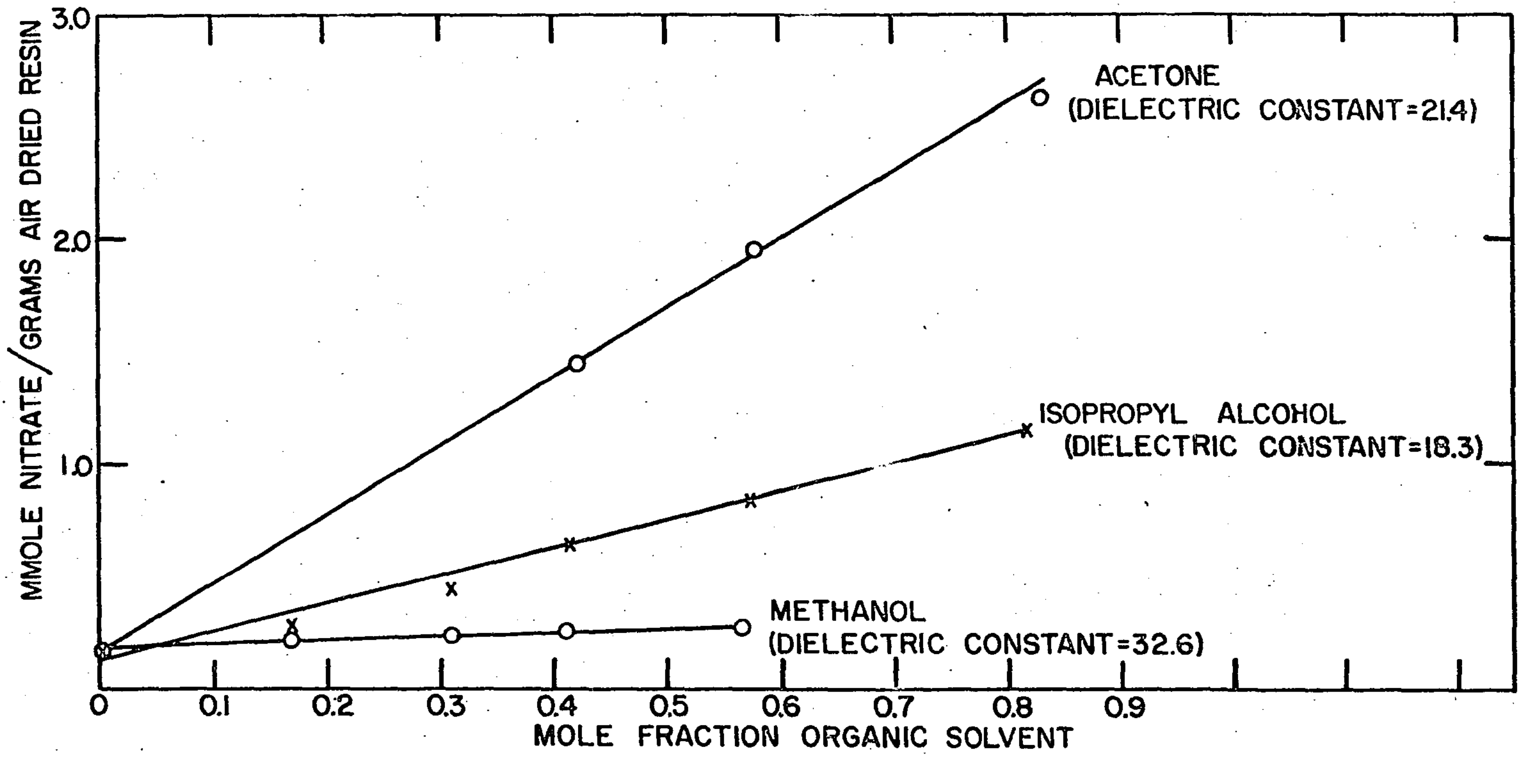


Figure 17. Sorption of lithium nitrate by Dowex 1-X8, 20-50 mesh resin as a function of mole fraction organic solvent from a 0.50M lithium nitrate solution

only the dielectric constants of the three solvents studied, one might expect the amount of invasion in acetone to be between methanol and isopropyl alcohol, with invasion being lowest in methanol and highest in isopropyl alcohol. Actually, it is higher in acetone than in methanol and isopropyl alcohol. Considering only the solubility argument, invasion occurs in the expected order. It is highest in acetone, in which lithium nitrate is the least soluble, and lowest in methanol, in which lithium nitrate is the most soluble. The increase of invasion with an increase in the solution concentration of lithium nitrate and nitric acid shown in Figure 17 and Table 17 can be explained using the Donnan potential concept and the above mentioned solubility argument.

Table 17. Sorption of lithium nitrate by Dowex 1-X8, 20-50 mesh resin as a function of mole fraction organic solvent from a 0.50M lithium nitrate solution

Mole fraction organic solvent	Mmoles nitrate / gram air dried resin		
	Acetone	Isopropyl alcohol	Methanol
0	0.160	0.163	0.165
0.165	-----	0.254	0.196
0.308	-----	0.462	0.236
0.422	1.47	0.643	0.236
0.575	1.94	0.860	0.268
0.822	2.62	1.16	-----

In Figure 16 and Table 16 it is not quite clear why the invasion of lithium nitrate is lower than nitric acid at low isopropyl alcohol concentrations and higher at high alcohol concentrations. The higher invasion of nitric acid can perhaps be related to the lower dissociation of nitric acid at low concentrations of electrolyte (32, pp. 731-732). The higher invasion of lithium nitrate at high alcohol contents might be related to the lower solutility of lithium nitrate than nitric acid in isopropyl alcohol.

Determination of Mean Ligand Numbers

It is often useful as well as interesting to know the nature of the species involved in particular ion exchange separations. Knowing this, one is in a better position to draw conclusions as to the actual mechanism of the ion exchange process. It was decided in this work to determine the mean ligand number of various metal ions with the nitrate ligand. This was done in both the solution phase and in the ion-exchange resin phase in equilibrium with the solution. The cation exchange method used in this work to study species in solution is a modification of the one developed by Fritz and Waki (33). The anion exchange method of these authors was also applied to the determination of the mean ligand number of metals inside anion-exchange resin.

The mean ligand number is defined as the average number of ligands per central atom in a complex. Mathematically, this can be expressed as

$$\bar{m} \text{ or } \bar{n} = \frac{C_L - [L]}{C_M} \qquad (8)$$

where $\bar{m}$ is the mean ligand number in solution, $\bar{n}$ the mean ligand number in the resin phase, C_L and C_M the analytical concentration of ligand and metal respectively, and [L] represents the equilibrium concentration of ligand.

The following derivations are worked out for use in a mixed water-organic solvent system in which the dissociation of acids is not complete, but the derivations are just as applicable in aqueous systems.

In both the resin and solution phase experiments, perchloric acid was used to maintain constant ionic strength and constant acidity. This was done by adding enough perchloric acid to a solution in which the concentration of nitric acid had been reduced to give the same solution conductivity as an original nitric acid solution containing no perchloric acid. This assumes that the mobility of the perchlorate ion and the nitrate ion are equal. They are not, but they are close enough so that the resultant error is small.

It also has to be assumed in these derivations that perchlorate complexes of the metals studied are nonexistant or negligibly weak. This is a good assumption in aqueous perchloric acid solutions but may be open to some question when using solutions containing high percentages of isopropyl alcohol, at least in the anion-exchange resin phase.

The following derivations are also worked out for a particular metal ion, manganese(II), using the nitrate ligand instead of for a general case. It is readily apparent how the final expressions would change for metals of different valences.

Solution phase derivation

The distribution of manganese(II) between a cation-exchange resin and a solution containing nitric acid is given by Equation 9.

$$D = \frac{[Mn^{+2}] + [Mn(NO_3^-)^+] + [Mn(NO_3^-)R] + [MnR]}{(Mn^{+2}) + (Mn(NO_3^-)^+) + (Mn(NO_3^-)_2^\circ) + ---(Mn(NO_3^-)_n^{\ 2-n})} \qquad (9)$$

In this equation [ ] represents concentration in the resin phase, ( ) represents concentration in the solution phase, and R represents a resin site. It is now assumed that at low concentrations of nitric acid invasion is low, so that the concentration of nitrate in the resin phase is low. Thus $[Mn(NO_3^-)^+]$ and $[Mn(NO_3^-)R]$ should be negligible.

Replacing terms in Equation 9 with their equilibrium formation constants and factoring out terms containing Mn^{+2} gives the following equation:

$$D = \frac{[Mn^{+2}]}{(Mn^{+2})} \cdot \frac{1 + \beta_{MnR}[R]}{1 + \beta_1(NO_3^-) + \beta_2(NO_3^-)^2 + --- \beta_n(NO_3^-)^n} \qquad (10)$$

Here β_{MnR} indicates $[MnR]/[Mn^{+2}][R]$. According to Donnan equilibrium $[Mn^{+2}]/(Mn^{+2})$ is proportioned to $[H^+]^2/(H^+)^2$ (31, p. 141). Thus

$$D = k\frac{[H^+]^2}{(H^+)^2} \cdot \frac{1 + \beta_{MnR}[R]}{1 + \beta_1(NO_3^-) + \beta_2(NO_3^-)^2 + ---} \qquad (11)$$

where k is an activity coefficient term. Experiments are performed at constant ionic strength and at constant acidity so k and $[H^+]^2/(H^+)^2$ are constant. Also $[R]$ is kept constant by using only small amounts of metal ion in the experiments. On taking the logarithm and derivative of both sides of Equation 11 the following results are obtained.

$$d \log D = d \log K \frac{[H^+]^2}{(H^+)^2} + d \log \left\{ 1 + \beta_{MnR} [R] \right\} - d \log \left\{ 1 + \beta_1 (NO_3^-) + \beta_2 (NO_3^-)^2 + --- \right\} \qquad (12)$$

Since the derivative of a constant is equal to zero

$$d \log D = - d \log \left\{ 1 + \beta_1 (NO_3^-) + \beta_2 (NO_3^-)^2 + --- \right\} \qquad (13)$$

It is convenient to use the analytical concentration of nitrate instead of the dissociated nitrate concentration. From the expression

$$(NO_3^-)_t + (NO_3^-) + (HNO_3) = (NO_3^-) \left\{ 1 + (H^+) \beta_{HNO_3} \right\} \qquad (14)$$

the term equal to (NO_3^-) replaces (NO_3^-) in Equation 13. Also the expression $\left\{ 1 + (H^+)\beta_{HNO_3} \right\}$ is equal to a constant, so $\frac{\beta 1}{1+(H^+)\beta_{HNO_3}}$ can be replaced by β_1' and $\frac{\beta 2}{1+(H\ )\beta_{HNO_3}}$ can be replaced by β_2', etc. This gives Equation 15.

$$d \log D = -d \log (1 + \beta_1' (NO_3^-)_t + \beta_2' (NO_3^-)_t^2 + ---) \qquad (15)$$

Since d log X = dx/x

$$d \log D = - \frac{(\beta_1' + 2\beta_2' (NO_3^-)_t + ---)\ d(NO_3^-)_t}{1 + \beta_1' (NO_3^-)_t + \beta_2' (NO_3^-)_t^2 + ---} . \qquad (16)$$

If both the numerator and denominator of Equation 16 are multiplied by $(NO_3^-)_t/(NO_3^-)_t$

$$d\ \log D = -\frac{\beta_1'(NO_3^-)_t + 2\beta_2'(NO_3^-)_t^2 + ---}{1 + \beta_1'(NO_3^-)_t + \beta_2'(NO_3^-)_t^2 + ---} \quad \frac{d(NO_3^-)_t}{(NO_3^-)_t} \qquad (17)$$

If $\beta_1'(NO_3)_t$, etc. in Equation 17 are replaced by their equivalents, Equation 18 results.

$$d\ \log D = -\frac{\frac{(Mn(NO_3^-)^+)}{(Mn^{+2})} + 2\frac{(Mn(NO_3^-)_2)}{(Mn^{+2})} + ---}{\frac{(Mn(NO_3^-)^+)}{(Mn^{+2})} + \frac{(Mn(NO_3^-)_2)}{(Mn^{+2})}} \cdot d\ \log(NO_3^-)_t \qquad (18)$$

If the numerator and denominator of Equation 18 are multiplied by (Mn^{+2}) and divided by d log $(NO_3^-)_t$, Equation 19 results.

$$\frac{d\ \log D}{d\ \log(NO_3^-)_t} = -\frac{(Mn(NO_3^-)^+) + 2(Mn(NO_3^-)_2) + ---}{(Mn^{+2}) + (Mn(NO_3^-)^+) + (Mn(NO_3^-)_2) + ---} \qquad (19)$$

Since the right side of Equation 19 is equal to $\bar{m}$,

$$\frac{d\ \log D}{d\ \log(NO_3^-)_t} = -\ \bar{m}. \qquad (20)$$

Thus $\bar{m}$ can be evaluated from the limiting slope at $[ClO_4^-] = 0$ of the curve log D vs. log $(NO_3^-)_t$. For best results, measurements should be done in tracer scale. This implies using very low loading of metal ion on the ion exchange resin, which means lower than at least one per cent of the ion exchange capacity. The reason for using low loads is because D values usually vary with loading. This is most serious at higher loads. It is caused by the variation of activity coefficients, the mass action effect, and sometimes by the formation of polymers. In this work loads higher than one percent were usually used. It is felt though that because the loading changed very little with changing concentrations of nitrate the resulting error was not serious. The mean ligand numbers are presented in Table 18 and other pertinent information in Table 19. The curves for the metals studied are shown in Figures 18-22.

Table 18. Mean ligand numbers of various metals

Element	Solvent	Mean ligand number	
		Solution phase, $\bar{m}$	Resin phase, $\bar{n}$
Pb(II)	0.50M HNO_3- 90% isopropyl alcohol	1.9	3.0
Mn(II)	0.50M HNO_3- 90% isopropyl alcohol	1.1	3.5
Yb(III)	1.50M HNO_3- 85% isopropyl alcohol	3.0	3.9
La(III)	1.50M HNO_3- 85% isopropyl alcohol	4.8	3.9
La(III)	1.50M HNO_3	0.7	4.8

Resin phase derivation

The distribution coefficient of manganese(II) between the anion-exchanger and a nitric acid solution can be written as follows:

$$D = \frac{[Mn^{+2}] + [Mn(NO_3^-)^+] + [Mn(NO_3^-)_2^0] + \text{---}[Mn(NO_3^-)_n^{2-n}]}{(Mn^{+2}) + (Mn(NO_3^-)^+) + (Mn(NO_3^-)_2^0)} \qquad (21)$$

where [ ] and ( ) indicate the concentrations in the resin phase and solution phase respectively. Replacing terms in Equation 21 with their equilibrium formation constants and

Table 19. Distribution coefficients as a function of nitric acid concentration at constant ionic strength using cation exchange resin

Metal ion	Ionic strength	Solvent	HNO_3 M	Distribution coefficient
La(III)	1.50	H_2O	1.50	44.7
			1.48	45.4
			1.46	45.7
			1.42	45.8
			1.38	48.3
La(III)	1.50	85% isopropyl alcohol 1.50M HNO_3	1.50	6850
			1.48	7500
			1.46	7800
			1.42	8650
			1.34	9600
Yb(III)	1.50	85% isopropyl alcohol 1.50M HNO_3	1.50	4325
			1.48	4580
			1.46	5230
			1.38	5525
			1.34	6000
Pb(II)	0.50	90% isoporpyl alcohol 0.50M HNO_3	0.50	3250
			0.48	3800
			0.46	4100
			0.44	4250
			0.42	4800
			0.40	5500
			0.38	6000
			0.36	7250
			0.34	6350
			0.30	9600
Mn(II)	0.50	90% isopropyl alcohol 0.50M HNO_3	0.48	8500
			0.46	8900
			0.44	9400
			0.42	9550
			0.36	10,650
			0.32	11,550

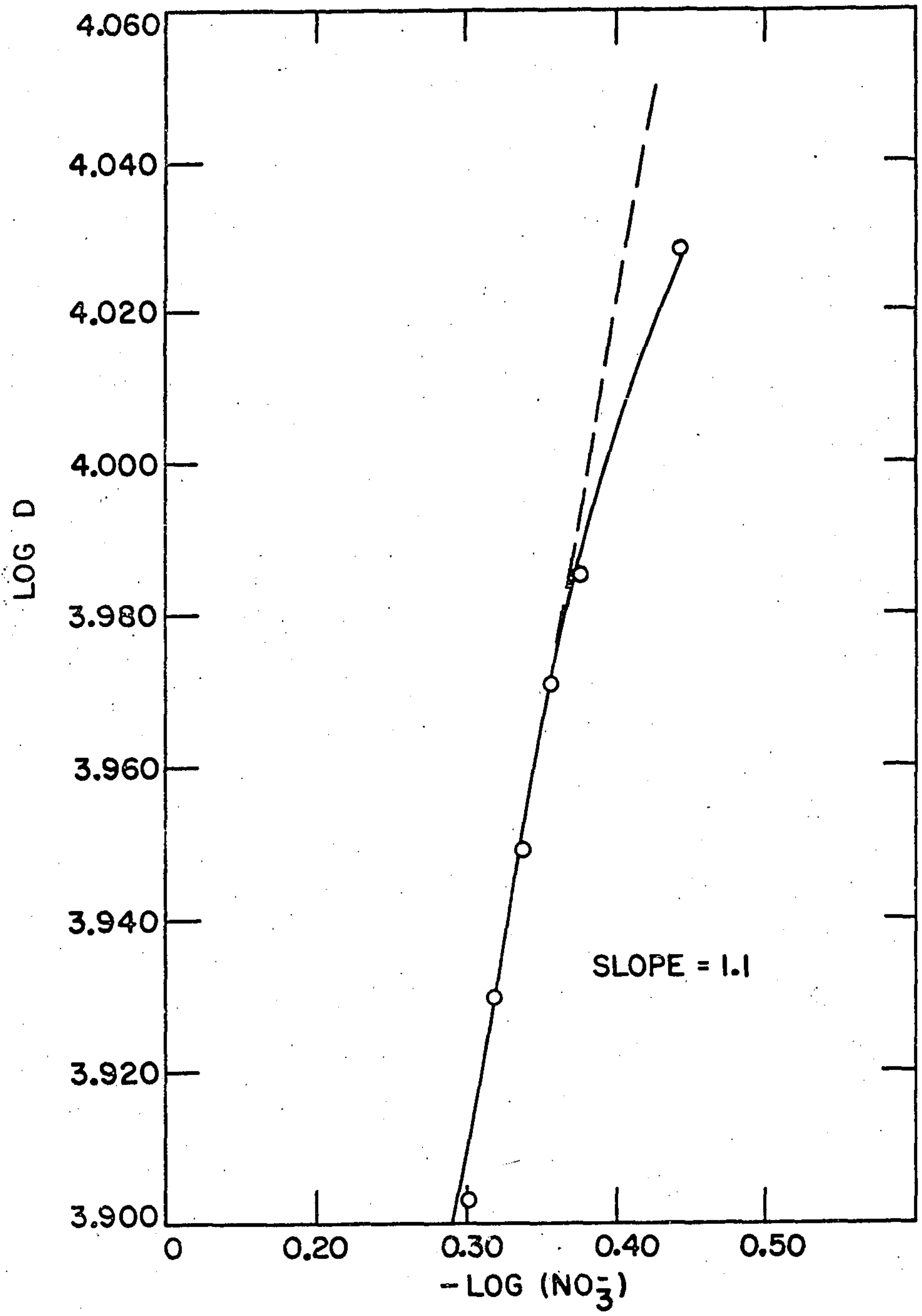


Figure 18. Determination of $\bar{m}$ for manganese(II) in a solution of 0.50M nitric acid-90% isopropyl alcohol by cation exchange techniques

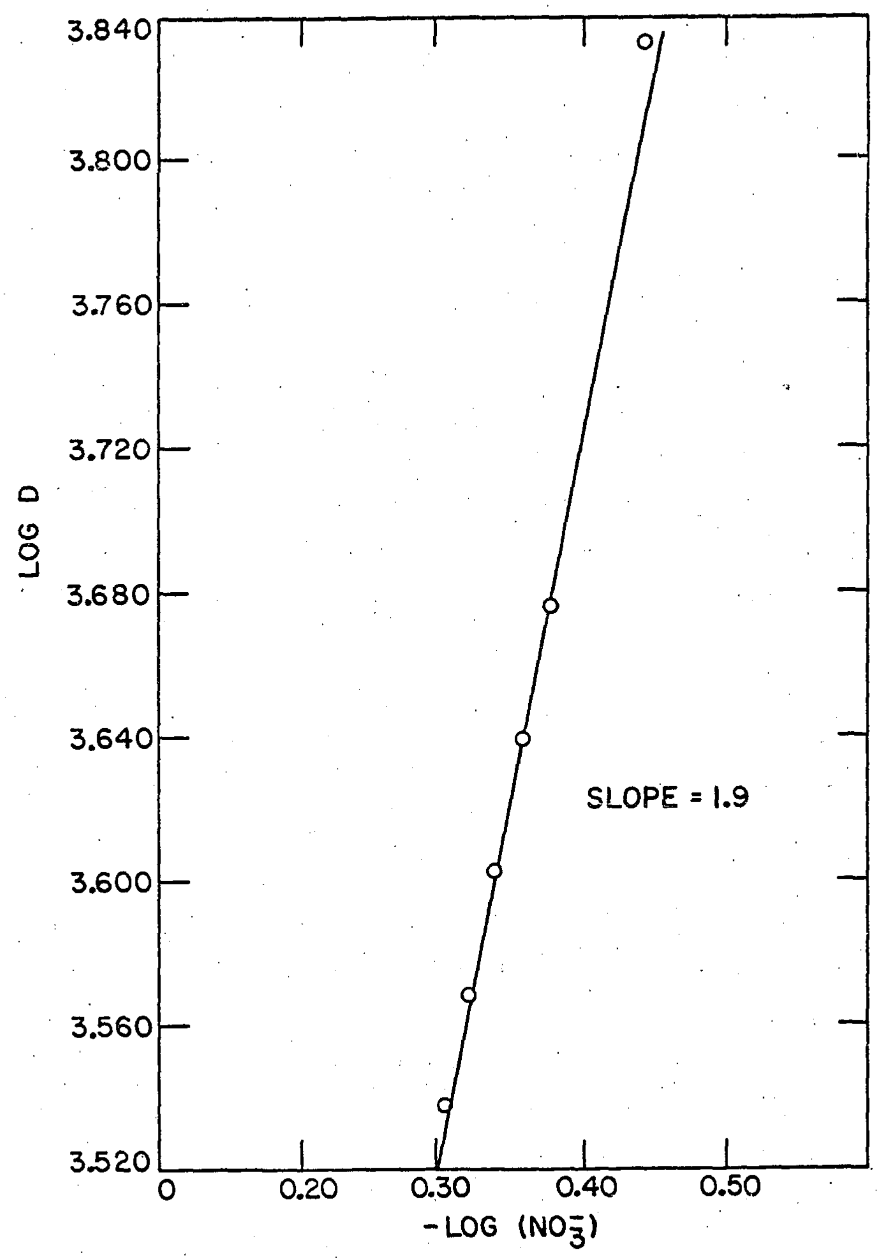


Figure 19. Determination of $\bar{m}$ for lead(II) in a solution of 0.50M nitric acid-90% isopropyl alcohol by cation exchange techniques

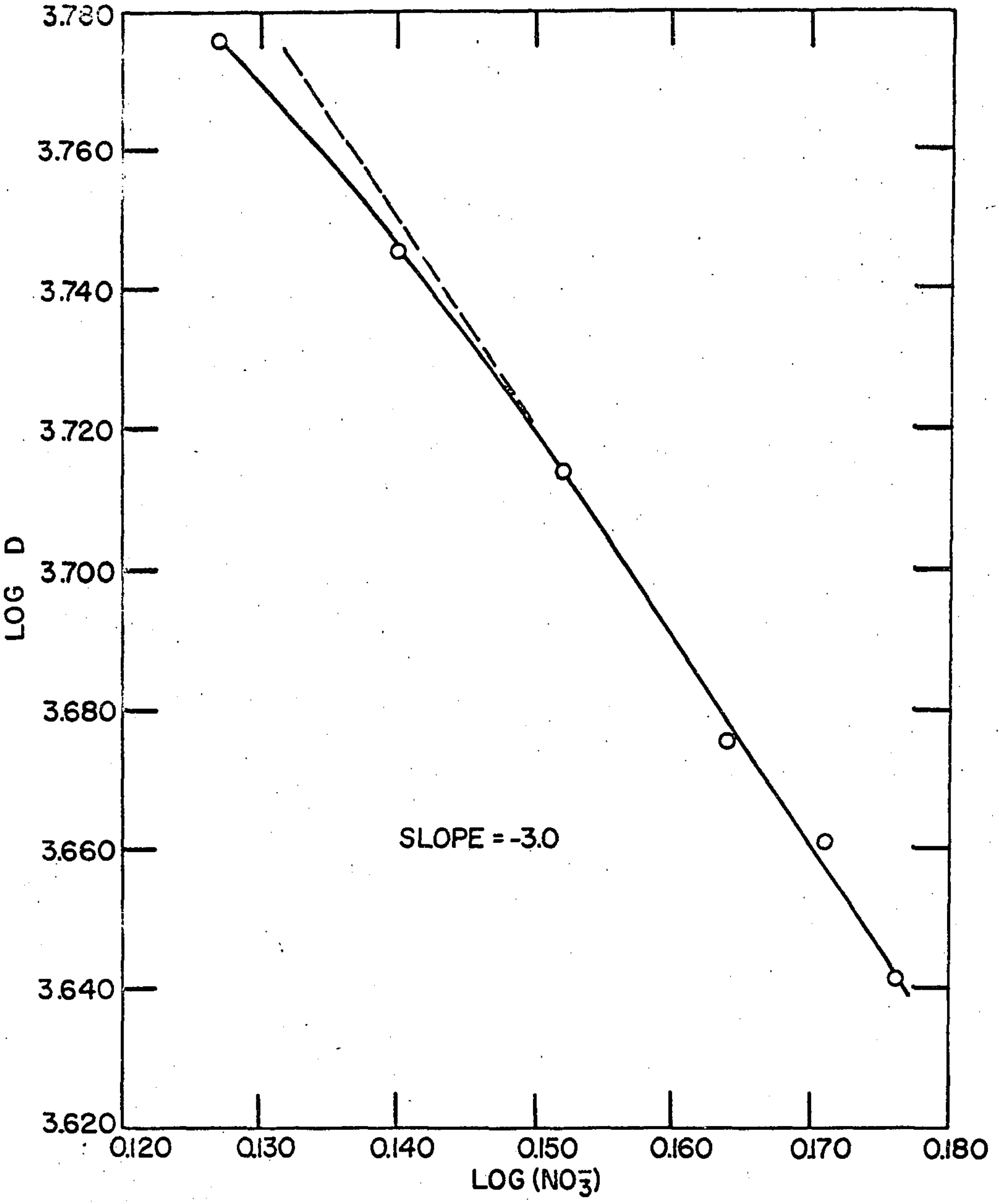


Figure 20. Determination of $\bar{m}$ for ytterbium(III) in a solution of 1.50M nitric acid-85% isopropyl alcohol by cation exchange techniques

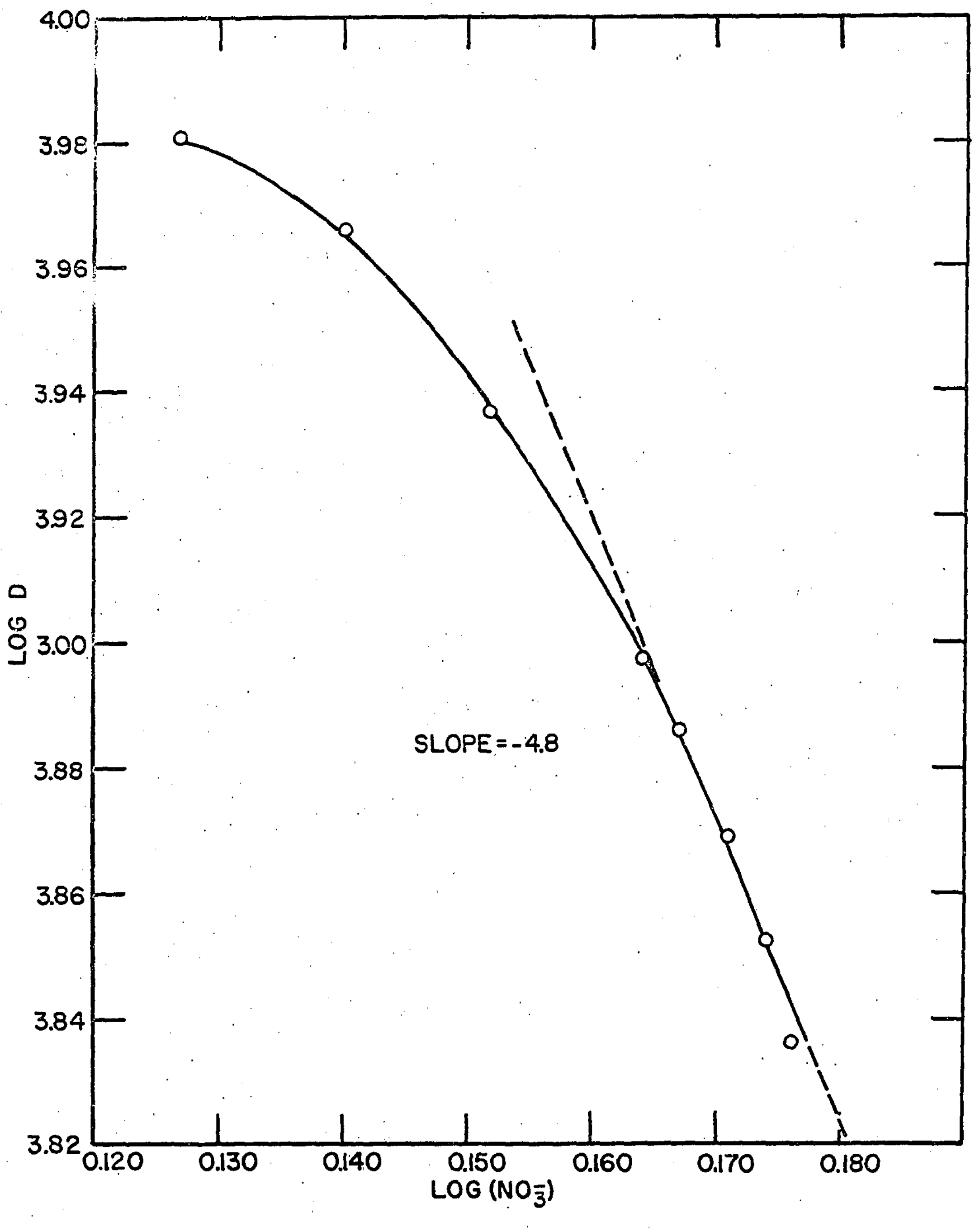
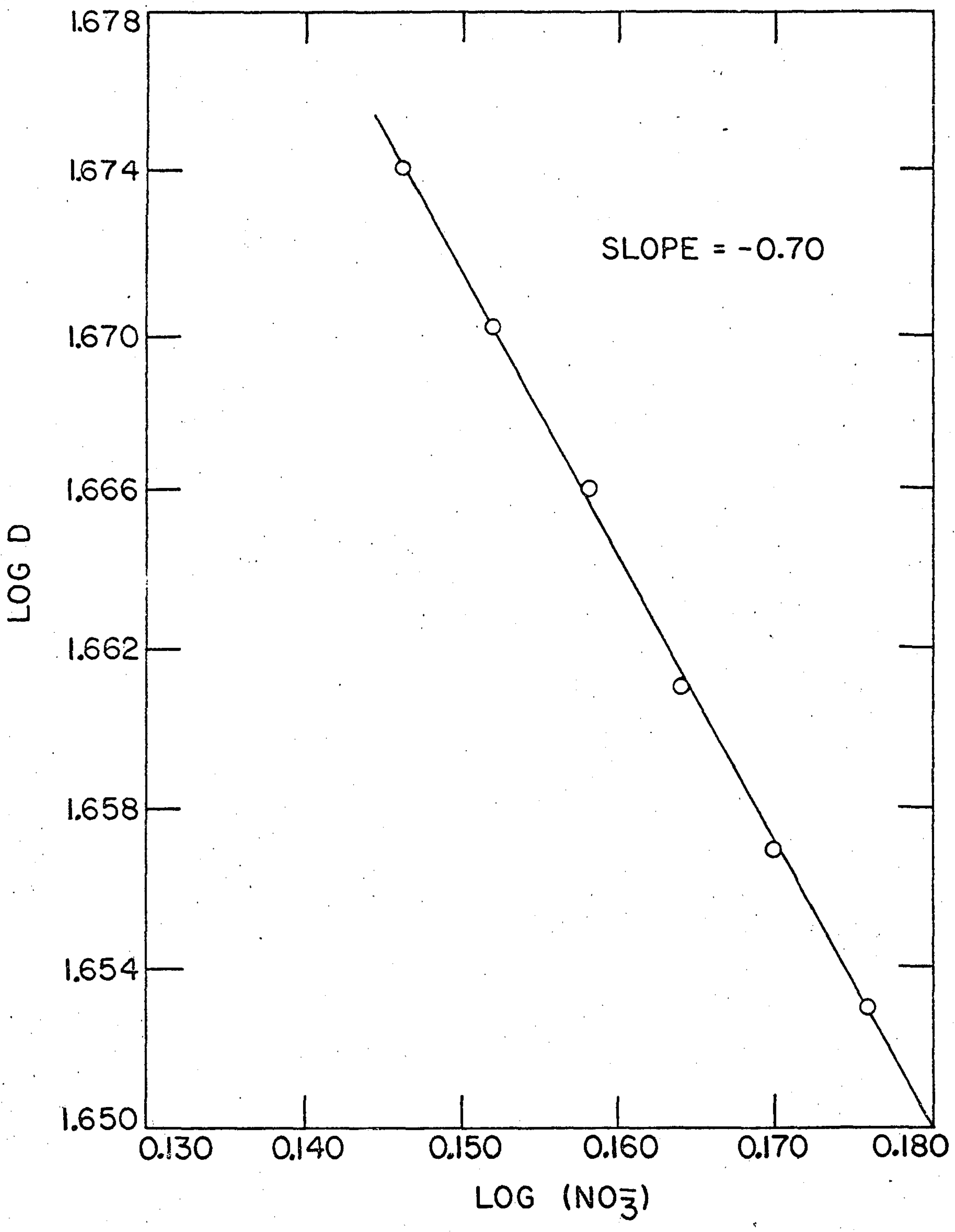


Figure 21. Determination of $\bar{m}$ for lanthanum(III) in a solution of 1.50M nitric acid-85% isopropyl alcohol by cation exchange techniques

Figure 22. Determination of $\bar{m}$ for lanthanum(III) in a solution of 1.50M nitric acid by cation exchange techniques


1.678
1.674
1.670
1.666
1.662
1.658
1.654
1.650
LOG D
0.130
0.140
0.150
0.160
0.170
0.180
LOG (NO_3^-)
SLOPE = -0.70

factoring out terms containing Mn^{+2} gives the following equation:

$$D = \frac{[Mn^{+2}]}{(Mn^{+2})} \cdot \frac{\left\{1 + \bar{\beta}_1[NO_3^-] + \bar{\beta}_2[NO_3^-]^2 + --- \bar{\beta}_n[NO_3^-]^n\right\}}{\left\{1 + \beta_1(NO_3^-) + \beta_2(NO_3^-)^2\right\}} . \qquad (22)$$

In Equation 22 $\bar{\beta}_1$ is defined as a stability constant of a nitrate complex for the resin phase. According to Donnan equilibrium $[Mn^{+2}]/(Mn^{+2})$ is proportional to $(NO_3^-)^2/[NO_3^-]^2$ (31, p. 141). Thus

$$D = \frac{k(NO_3^-)^2}{[NO_3^-]^2} \cdot \frac{\left\{1 + \bar{\beta}_1[NO_3^-] + \bar{\beta}_2[NO_3^-]^2 + ---\right\}}{\left\{1 + \beta_1(NO_3^-) + \beta_2(NO_3^-)^2\right\}} \qquad (23)$$

where k is an activity coefficient term. As in the solution phase analysis it is convenient to use the analytical concentration nitrate instead of the dissociated nitrate concentration. Making the same substitutions as in the solution phase analysis for (NO_3^-) in Equation 23 gives

$$D = k\,\frac{(NO_3^-)_t^2}{[NO_3^-]_t^2} \cdot \frac{\left\{1 + \bar{\beta}_{HNO_3}[H^+]\right\}^2}{\left\{1 + \beta_{HNO_3}(H^+)\right\}^2} \cdot \qquad (24)$$

$$\frac{\left\{1 + \bar{\beta}_1'[NO_3^-]_t + \bar{\beta}_2'[NO_3^-]^2 + ---\right\}}{\left\{1 + \beta_1'(NO_3^-)_t + \beta_2'(NO_3^-)_t^2\right\}} .$$

When the experiments are run at constant ionic strength and constant acid strength $\bar{\beta}_{HNO_3}$, $[H^+]$, and (H^+) are all constant. Thus on taking the logarithm and the derivation of both sides of Equation 24, the following equation results:

$$d \log D = 2\, d \log (NO_3^-)_t + d \log \left\{ 1 + \bar{\beta}_1'[NO_3^-]_t + \bar{\beta}_2'[NO_3^-]_t + --- \right\} - 2\, d \log [NO_3^-]_t - d \log \left\{ 1 + \beta_1'(NO_3^-)_t + \beta_2'(NO_3^-)_t^2 \right. . \qquad (25)$$

The term $d \log \left\{ 1 + \beta_1'(NO_3^-)_t + \beta_2'(NO_3^-)_t^2 \right\}$, as shown in the solution phase derivation, is equal to $\bar{m}\, d \log (NO_3^-)_t$. Likewise the term $d \log \left\{ 1 + \bar{\beta}_1'[NO_3^-]_t + \bar{\beta}_2'[NO_3^-]^2 \right\}$ is equal to $\bar{n}\, d \log [NO_3^-]_t$. Substituting these terms in Equation 25 and rearranging gives

$$d \log D + \bar{m}\, d \log (NO_3^-)_t - 2\, d \log (NO_3^-)_t = \bar{n}\, d \log [NO_3^-]_t - 2\, d \log [NO_3^-]_t . \qquad (26)$$

Dividing both sides of Equation 26 by $d \log [NO_3^-]_t$ and rearranging gives the final result shown below:

$$\frac{d \left\{ \log D + (\bar{m}-2) \log (NO_3^-)_t \right\}}{d \log [NO_3^-]_t} = \bar{n} - 2 \qquad (27)$$

Thus $\bar{n}$ can be evaluated from the limiting slopes at $[ClO_4^-] = 0$ of the curve $\log D + (\bar{m}-2) \log (NO_3^-)_t$ vs. $\log [NO_3^-]_t$. The quantity $[NO_3^-]_t$ refers to the summation of $[NO_3^-]$ and $[HNO_3]$ and excludes the nitrate ions combined with the metal ion. When the load of metal ion becomes significantly high, correction must be made for the nitrate ions in the various complexes present. This is done by first determining an approximate ligand number, $\bar{n}^*$, using the total nitrate concentration including the nitrates from complexes, $[NO_3^-]_t^*$. The true $(NO_3^-)_t$ is then obtained from the following equation:

$$\left[NO_3^-\right]_t = \left[NO_3^-\right]_t^* - \bar{n}^* \left[Mn^{+2}\right]_t \ . \qquad (28)$$

The true value of $\bar{n}$ is then calculated using $\left[NO_3^-\right]_t$. These values are presented in Table 18. Other pertinent information is in Table 20. The curves for the metals studies are shown in Figures 23-27.

It should be pointed out here that the distribution coefficients used in drawing the curves for the determination of mean ligand numbers are taken from smooth curves drawn through the experimental values of distribution coefficients plotted against nitrate concentration.

It is clear from Table 18 that complexes do not have to be anionic to be sorbed on anion exchange resin. Stability constants for manganese(II)$\left[\beta_1' = 2.8,\ \beta_2' = 2.8\right]$, determined by a curve-fitting technique, show that twenty percent of the manganese(II) is present as neutral species and the other eighty percent present as cationic species. Since positive species are excluded from anion exchange resin because of the Donnan potential, it is likely that only the neutral manganese(II) nitrate specie is being sorbed by the resin. On entering the resin phase, it then undergoes further complexation apparently to give mainly anionic species, which can be sorbed by the cationic resin sites.

Lanthanum(III) in the isopropyl alcohol-nitric acid solvent appears to have a higher ligand number in solution than in the resin phase. It is felt that this anomaly is

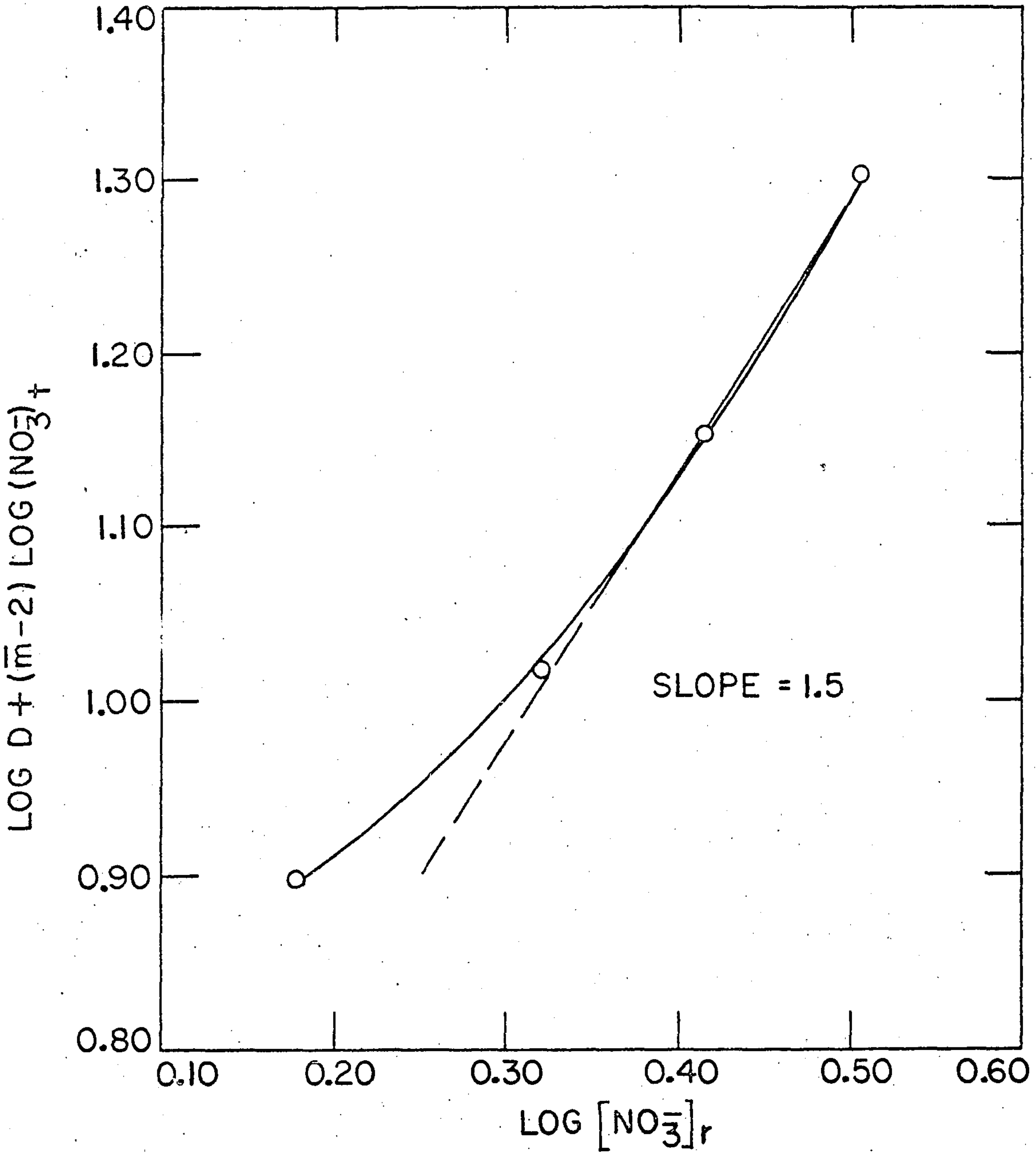


Figure 23. Curve for determination of $\bar{n}$ for manganese (II) in a solution of 0.50M nitric acid-90% isopropyl alcohol

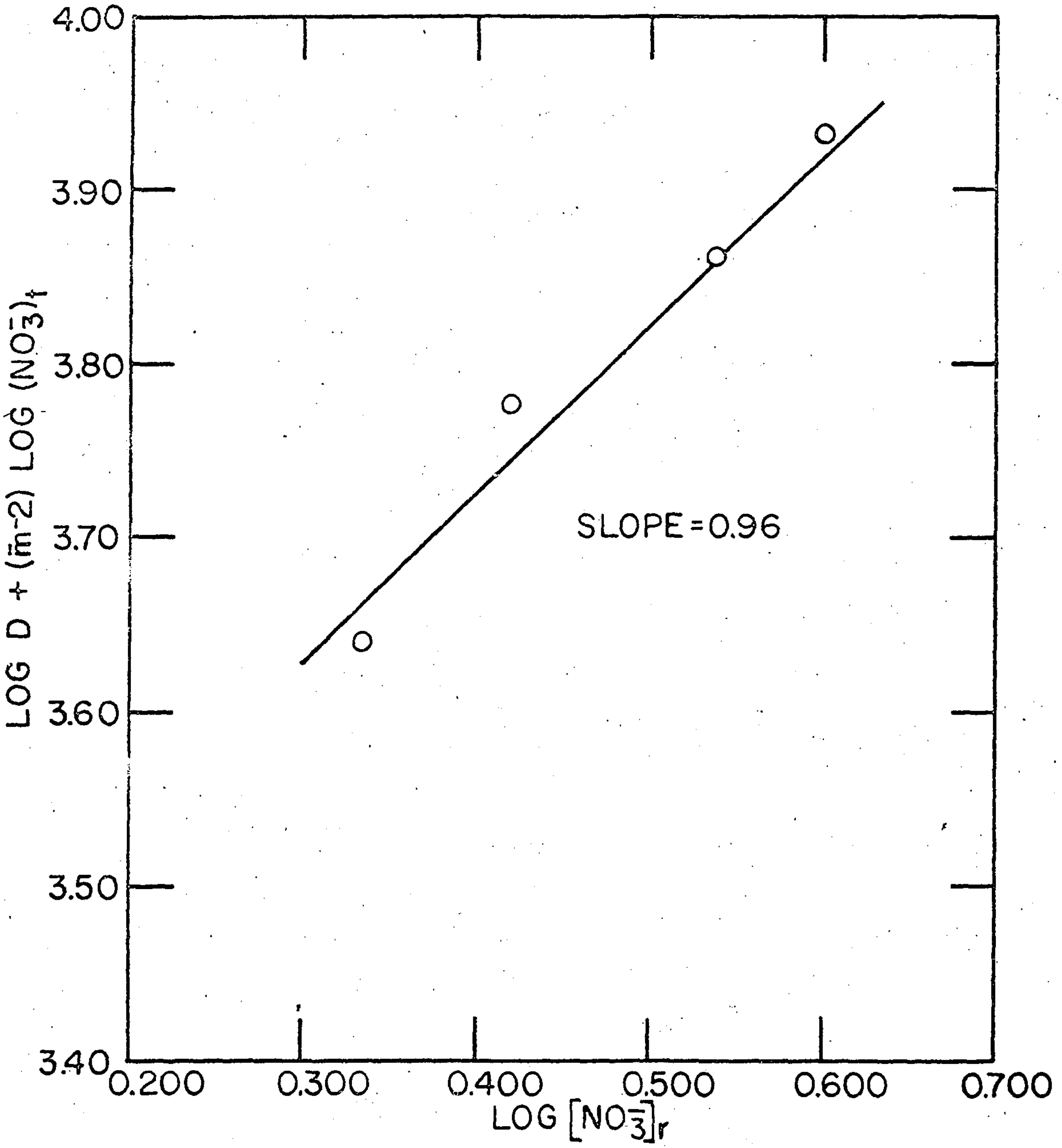
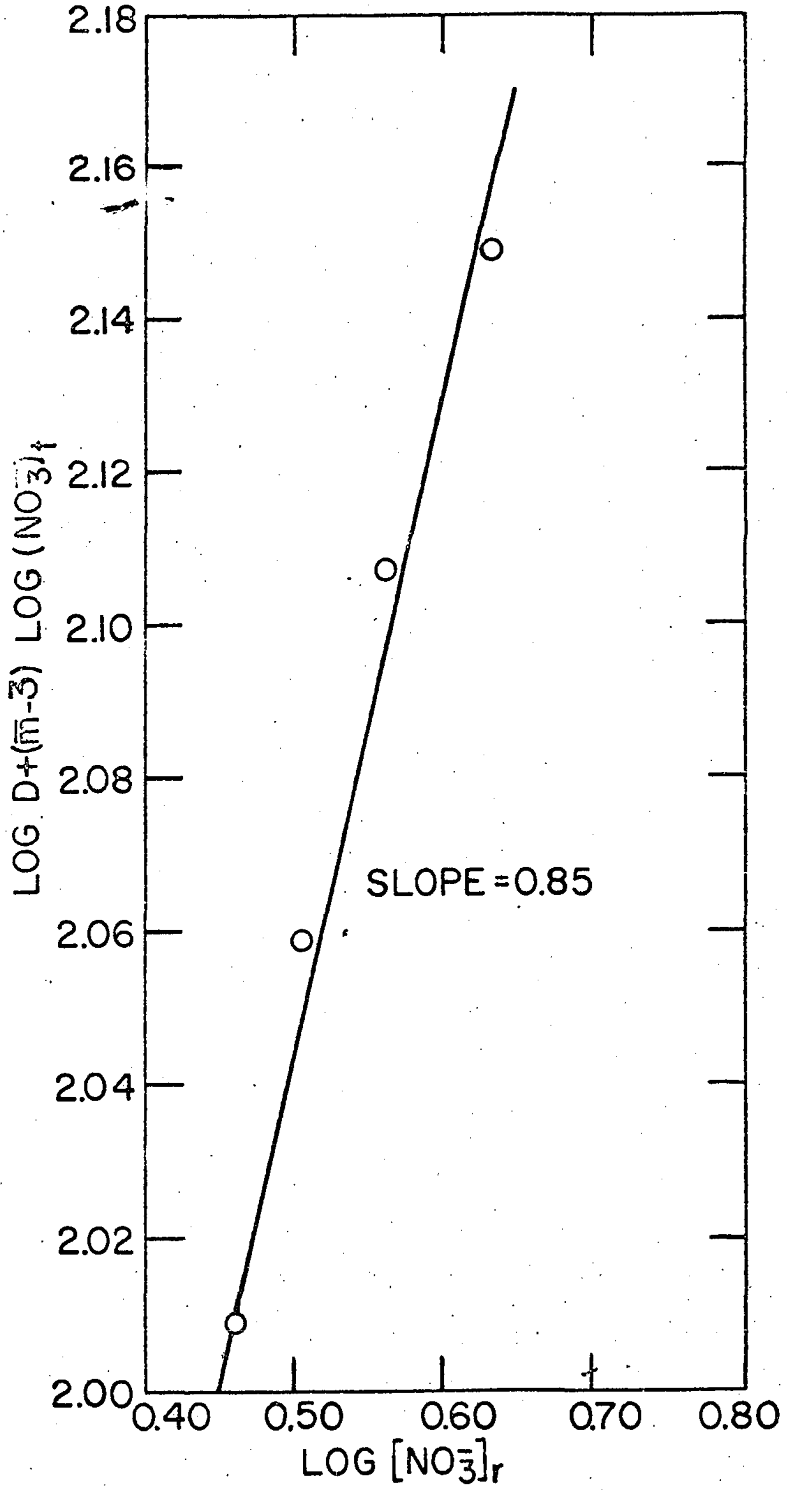


Figure 24. Curve for the determination of $\bar{n}$ for lead (II) in a solution of 0.50M nitric acid-90% isopropyl alcohol

Figure 25. Curve for determination of $\bar{n}$ for ytterbium(III) in a solution of 1.50M nitric acid-85% isopropyl alcohol


2.18
2.16
2.14
2.12
2.10
2.08
2.06
2.04
2.02
2.00
LOG D+($\bar{m}$-3) LOG $(NO_3^-)_f$
SLOPE = 0.85
0.40
0.50
0.60
0.70
0.80
LOG $[NO_3^-]_r$

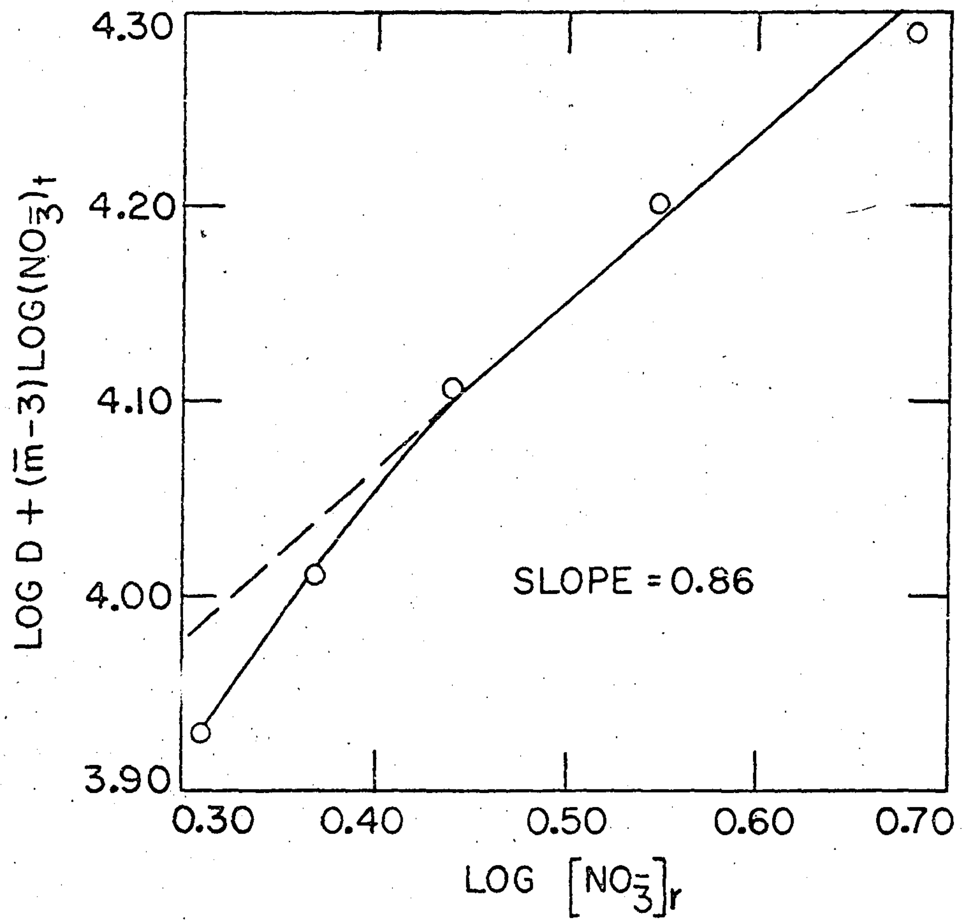


Figure 26. Curve for determination of $\bar{n}$ for lanthanum(III) in a solution of 1.50M nitric acid-85% isopropyl alcohol

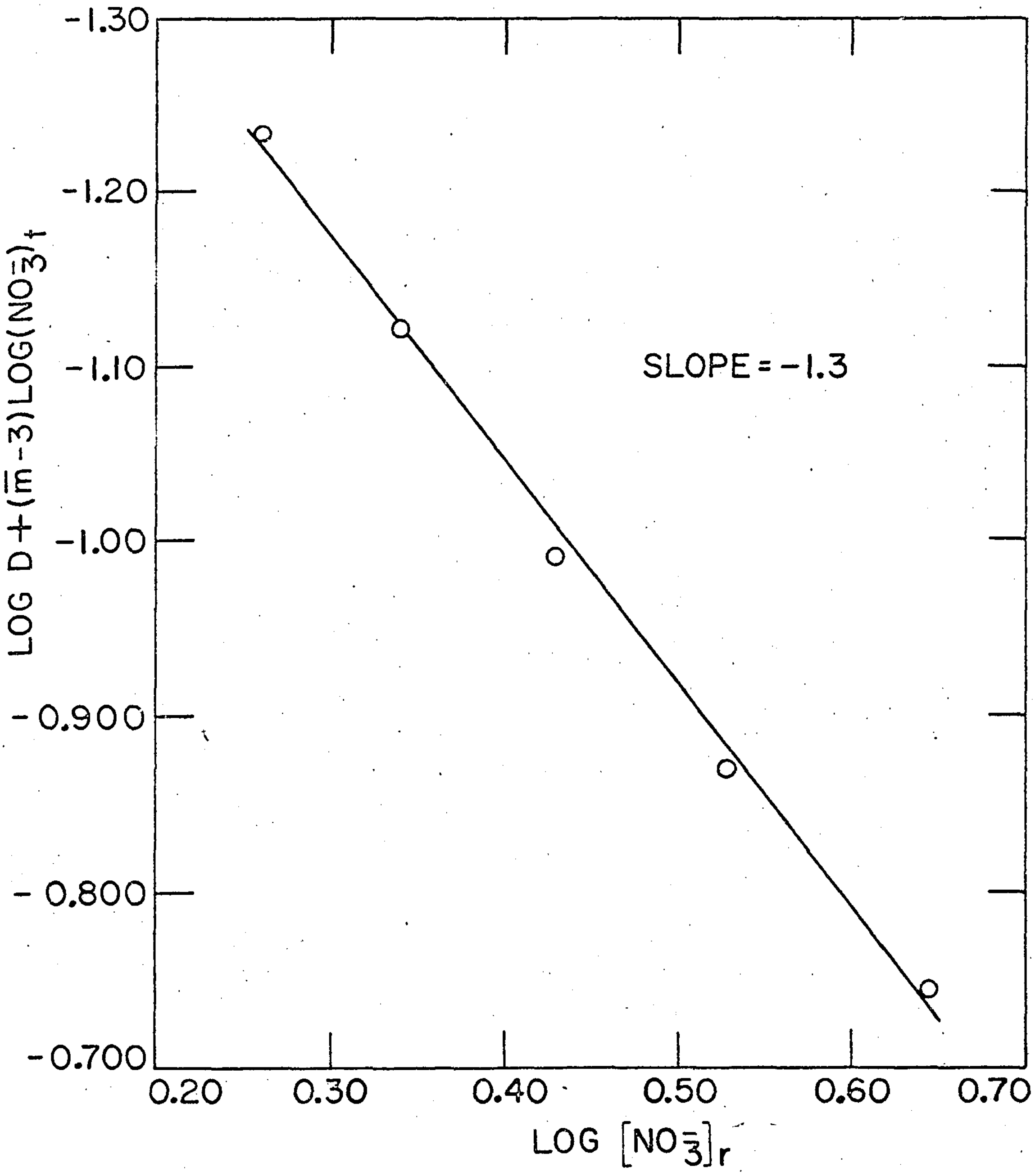


Figure 27. Curve for determination of $\bar{n}$ for lanthanum (III) in a solution of 1.50M nitric acid

probably due to the inaccuracy of the experimental data, which results in the mean ligand numbers being in error by about ten percent or more.

It is interesting to observe that the order of sorption of the metal ions of the same valence on the anion-exchange resin follows quite well with the order of sizes of the mean ligand numbers of the metals in solution. This does not appear to be true for the resin phase.

Another interesting observation is the greater closeness of ligand numbers in the resin phase compared to the solution phase.

Another fact worth observing is that the mean ligand numbers in the resin phase do not indicate that all or most of the metal ions have reached their saturation coordination numbers with respect to nitrate. This conflicts with the viewpoint held by some chemists (31, p. 233).

Finally, an obvious conclusion to be drawn from observing the mean ligand numbers in solution is that the strength of the nitrate complexes of the metals studied greatly increases in going from an aqueous solution to an isopropyl alcohol solution of nitric acid. An increase in strength is expected but it is interesting that the increase is as much as indicated by Table 18.

Table 20. Data for the determination of $\bar{n}$ for various metals using anion exchange resin

Metal ion	Ionic strength	Solvent	HNO_3 M	$[NO_3^-]_r$ $\frac{\text{mmole}}{\text{gram resin}}$	Distribution coefficient
Pb(II)	0.50	90% isopropyl alcohol 0.50M nitric acid	0.49	3.20	7250
			0.48	2.45	----
			0.47	2.22	4350
			0.46	1.72	2700
Mn(II)	0.50	90% isopropyl alcohol 0.50M nitric acid	0.50	3.20	10
			0.49	2.60	7.0
			0.48	2.10	5.0
			0.47	1.73	3.7
			0.46	1.51	---
Yb(III)	1.50	85% isopropyl alcohol 1.50M nitric acid	1.50	5.33	---
			1.48	4.34	139
			1.46	3.69	132
			1.44	3.24	114
			1.42	2.94	102
La(III)	1.50	85% isopropyl alcohol 1.50M nitric acid	1.50	5.04	9360
			1.47	3.51	7950
			1.44	2.84	6650
			1.41	2.51	5550
			1.38	2.10	4730
La(III)	1.50	1.50M nitric acid	1.50	4.44	0.458
			1.48	3.37	0.323
			1.46	2.69	0.243
			1.44	2.19	0.181
			1.42	1.82	0.131

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