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# ANION EXCHANGE SEPARATIONS OF METAL IONS IN PARTIALLY NONAQUEOUS SOLUTIONS

by

Donald John Pietrzyk

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# INTRODUCTION

The phenomenon of ion exchange has been recognized since the middle of the 19th century (1, 2). Many of the early scientific investigations were carried out with clays and minerals. Among the minerals that attracted the attention of scientists were the zeolites. These can be regarded as built up by an alumino-silicate skeleton together with a sufficient number of exchangeable cations such as sodium (I), potassium (I), magnesium (II), or calcium (II). At the turn of the century artificial silicates were prepared and have been successfully used on a large scale for water softening.

The ion exchange properties of many natural organic materials such as cellulose and coal were also studied. However, applications were few because their capacities are low and their acidic groups are ionized only in alkaline solutions.

Since 1935 there have been two parallel developments of organic exchangers. In one case, many processes have been patented for modifying the properties of the natural materials. In the other, a large number of artificial resins of suitable structure have been synthesized in the laboratory.

The first synthetic ion-exchange resins were prepared by two English chemists, B. A. Adams and E. L. Holmes (3), in 1935. Both cation and anion exchange resins were prepared and their combined use for total removal of salts was demonstrated. The cation resin was synthesized via the condensation of a dihydric phenol and formaldehyde, followed by sulfonation. The anion resin was a condensation product of m-phenylenediamine and formaldehyde. The acidic $-SO_3H$ group in the former and the basic $-NH_2$ group in the latter are the exchangeable centers.

This classical pioneer work of Adams and Holmes laid the ground work for the production of the high capacity and selective resins in use today. The strongly acidic cation exchange resins and strongly basic anion exchange resins in current use are prepared from polystyrene which has been crosslinked with a specified amount of divinylbenzene. The crosslinked polystyrene is sulfonated to introduce the $-SO_3H$ group for the cation resin. In the preparation of the anion resin the crosslinked polystyrene is first chloromethylated and then converted to a quaternary amine (exchange center) by reaction with a tertiary amine. Of utmost importance is the synthesis of the anion resin since the applications of previous anion exchangers were seriously limited owing to a lack of high capacity and good stability.

The widespread availability of relatively cheap and stable synthetic ion exchangers of high capacity has played an important role in analytical chemistry. The analyst has used the ion exchange technique for the concentration of electrolytes, fractionation of ions, removal of interfering ions, preparation of reagents, the dissolution of insoluble electrolytes, and separation of organic and biochemical substances. Of prime importance is the ability to attain a rapid, complete separation of one metal from another or from a complex mixture. Of equal importance is the separation of multicomponent systems into less complex mixtures.

The rapid development of this analytical technique, which has taken place during the last two decades, was undoubtedly sparked by the availability of the resin and the application of chromatographic separations for similar elements. The chromatographic technique was introduced by Spedding _et al_. (4-10) and Ketelle and Boyd (11, 12) in 1947 for the separation of the rare earths. Elution, after adsorption of the rare earths on a strong cation resin in the hydrogen form, was with a dilute solution of citric acid at a low pH. The separation was later improved by using a copper (II) form resin and eluting with EDTA [(ethylenedinitrilo) tetraacetic acid] (13).

Following the rare earth work the chromatographic technique was used for the separation of other groups of similar elements. The alkali metals (14-16), alkaline earths (16-18), zirconium and hafnium (19-22), and the trans-uranic (actinide) elements (23, 24) were separated. Similarly, the halides (16, 25, 26) and condensed phosphates (ortho-, pyro-, tri-, trimeta-, and tetrametaphosphates) 27-29) were separated.

The technique has also been employed for the separation of organic materials on ion exchange resins. Moore and Stein

(30-32) successfully separated a synthetic mixture of 50 amino acids and related compounds. More recently, Rieman and his group (33-37) developed the technique "salting out chromatography" for the separation of water-soluble non-electrolytes with ion exchange resins and aqueous salt solutions. Calculations based on plate theory were used extensively to predict conditions for the separations.

The time necessary for any separation is closely related to the adsorbability ratios of the materials. In analytical work the time element is often the determining factor in selection of a separation scheme. For this reason the adsorbability ratio may often be altered to a more favorable value by taking advantage of the solution chemistry of the materials to be separated. Not only is the time element improved but also new avenues for separations are opened. Advantage can be taken of such properties as complexing reactions and specific acid-base reactions. Essentially, these are devices for altering the effective charge of the ions.

Reactions which would accentuate differences between metals are those which lead to formation of negatively charged complexes. The charge may not only be altered but actually reversed. Thus metal separations may become as simple as anions from cations.

Apparently the use of anion exchange for the recovery of metals was first suggested in 1945 by Sussman et al. (38) in connection with those elements which normally occur as negatively charged ions in solution. In 1948 Kraus, Nelson, and associates (39, 40) initiated the first complete study of the behavior of metal ions on a strongly basic anion exchange resin. In the presence of hydrochloric acid many elements which were considered not to form strong negatively charged complexes were found to adsorb on the resin. By adjustment of the eluting medium so that the concentration of adsorbed complex was drastically decreased these elements could then be removed systematically.

The adsorbabilities or distribution coefficients were measured for practically every metal over a range of 0.1 to 12 M hydrochloric acid. In many cases, several oxidation states of the same metal were also studied. Graphs were made of the distribution coefficient vs. concentration of hydrochloric acid for each of the elements. Also from this data, a table was prepared which gives the approximate elution order of the metallic elements and the proper concentration of hydrochloric acid to use for their elution. The curves and the table, being so complete, have proven to be of tremendous value to the analyst as it is a relatively simple matter for him to decide if this scheme is applicable to his separation problem. This study has been extended by the use of metal chloride salts in the eluting medium.

The basic procedure is to load the sample onto the anion exchange column out of strong hydrochloric acid. By decreasing the concentration of hydrochloric acid in the eluent one metal is eluted from the remainder. The eluent concentration is decreased again and another metal is eluted. This process is repeated until the separation is complete. Some typical examples to illustrate the broad scope of the method are the separation of the following mixtures: Ni(II)-Mn(II)-Co(II)-Cu(II)-Fe(III)-Zn(II), V(IV)-Ti(IV)-Fe(III), and As(V)-As(III) as done by Kraus and Nelson (39). In each case the order of elution is given and progressively weaker hydrochloric acid is used as eluent. Similarly, Wilkens and Hibbs (41-45) have used this scheme extensively in the determination of metals in various alloys. Berman and McBryde (46, 47) measured the distribution coefficients of the platinium metals by a similar technique and used these data for their separation.

The theoretical aspects of the adsorption have been discussed by Horne et al. (48-50), Marcus (51-53), and Herber and Irvine (54).

Because of the polymerization or precipitation tendencies of several elements in the 4th and 5th group, even at high acidities, the hydrochloric acid elution scheme has been modified by the addition of hydrofluoric acid. The fluoride ion serves as an effective ligand for inhibiting these hydrolytic reactions. Studies similar to the hydrochloric acid investigation have been carried out for the hydrofluoric-hydrochloric acid mixed system by Kraus et al. (39, 40, 55-58) and others

(59-62). This system has also been used extensively for separations, particularly if the mixture contains the 4th and/or 5th group elements. A prime example of the utility of this method is the complete separation of an eleven component high temperature alloy (63). Other alloys have also been separated by this scheme (64, 65).

Many other inorganic ligands have been used for anion exchange separations. Among these are the sulfate, nitrate, iodide, thiocyanate, bromide, phosphate, and cyanide ions. The principal feature of some of these anions is the selectivity, because only a few elements may be significantly adsorbed. Sulfate and nitrate ion exhibit this for uranium (VI) and thorium (IV) (39).

It has not been the author's intention to present a comprehensive review of the rapidly expanding applications of cation and anion exchange resins. What has been done, however, is to point out the pioneer work in this field. Fortunately, the ion exchange field, both theoretical and applications, is frequently reviewed and references to the large number of current publications are readily available (66-75).

## EFFECT OF ORGANIC SOLVENTS ON ION EXCHANGE

Articles describing the use of synthetic ion exchange resins in nonaqueous or mixed solvents have appeared principally in the past nine or ten years. However, the number of publications has been small compared to those dealing with aqueous ion exchange. Much of the early nonaqueous investigations were concerned with the effects of organic solvents on exchange equilibrium.

Regardless of solvent the exchange of univalent ions may be represented by the following equation,

$$(A^+)_o + (B^+)_i = (A^+)_i + (B^+)_o \qquad (1)$$

where $A^+$ and $B^+$ represent the ions being exchanged and i and o represent the resin and outside solution phase, respectively. For this reaction the equilibrium quotient involving ion activities, a, may be written as:

$$K_B^A = \frac{a(A^+)_i a(B^+)_o}{a(A^+)_o a(B^+)_i} \qquad (2)$$

If the activity coefficients are neglected the expression for the equilibrium quotient or selectivity coefficient will be

$$K_B^A = \frac{x(A^+)_i c(B^+)_o}{x(B^+)_i c(A^+)_o} \qquad (3)$$

where x is the mole fraction of the ion in the resin phase and c is the molar concentration of the ion in the solution phase.

The equilibrium quotient, K, is not a constant because it will vary with the percent loading on the resin and the percent cross-linking. If these properties are held constant a selectivity scale can be set up. This has been done with the univalent cations. Lithium (I) was taken as unity since it is the least preferred by the resin.

This approach to the investigation of ion exchange equilibria has been applied to exchange in nonaqueous and mixed solvents. From the inspection of the data that are available it appears that the selectivity coefficient for the exchange of a given pair of ions is usually greater when the ions are dissolved in an organic solvent of lower dielectric constant than water. The coefficient is usually greater when mixed solvents are used than when the solvent is either pure component. Methyl alcohol, ethyl alcohol, isopropyl alcohol, acetone, and dioxane and mixtures of these with water as well as mixed organic solvents have been used in these investigations. Most of these studies have been with the univalent cations and strongly acidic types of resins. Much of this previous work on cation resins has been reviewed by Bonner (76) and Fessler (77). Additional work has been reported for exchange equilibria on anion exchange resins (78, 79).

Several investigators have correlated this enhancement of selectivity coefficient to the dielectric constant (80-82). Davydov and Skoblionok (83) singled this out as the most important factor affecting the exchange efficiency. The solubility of salts, their dissociation, and the behavior of the ions depends largely on the dielectric constant of the solvent.

Rates of exchange are generally slower in nonaqueous media necessitating slower flow rates in column operations. As the polarity of a solvent decreases the exchange rate will decrease. Chance et al. (84) observed the exchange of sodium bromide with anion and cation resins in eight different solvents. All exchanges were slower than in water solutions. However, only a few were unreasonably slow.

Ion exchange resins absorb significant amounts of solvent in addition to their ability to remove ionic substances. This has been investigated by Gregor et al. (85) and Davies and Owen (86). Water mixtures of methyl alcohol, ethyl alcohol, isopropyl alcohol, dioxane, and acetone and their absorption effects on cation exchange resins were studied. It was found that the more polar solvent, water, is preferentially absorbed, the degree of preference being greatest at lower water content. The absorption is a function of the ionic form of the resin, the dielectric constant of each solvent, and the ability of the resin to swell. Because the solvent does participate in this manner, it has an important effect on any other ion exchange or adsorption process taking place within the resin.

Swelling properties of a strong cation resin in different forms [hydrogen(I), sodium(I), silver(I), and ammonium(I)] were observed by Gable and Strobel (87) in pure water and pure methyl alcohol. In all cases, the ratio of swollen volume to dry volume was less for the methyl alcohol solvent. It was concluded that because of the small swelling the solvent-ion interaction is probably small, and that there might be considerable ion pair formation between cations and the resin sulfonate ions.

Because less polar solvents produce less swelling, the resin is not as porous to ions or molecules in these solvents as in water. Thus, the capacity of the resin may be significantly lower. Bodamer and Kunin (88) determined the capacity of a strong cation resin in a variety of solvents, ethyl alcohol, acetone, dioxane, benzene, and gulf oil 361. The values were found to be nearly as high as in aqueous solutions. When the capacity of a series of anion resins for acetic acid was determined in these same solvents, the more porous resins had higher capacities. All of the resins except one had higher capacities in benzene and Gulf Oil 361 than in water by a factor of up to four times. The interpretation given was that four acetic acid molecules are absorbed for every functional group on the resin. This could be pictured as a clustering of the polar acetic acid molecules about the polar functional groups of the resin without actually having the usual ionic bonds established. For further evidence of this, when the resin is washed with a more polar solvent, 50-50 ethyl alcohol-benzene mixture, acetic acid is washed off until the resin contains less than one acetic acid molecule per functional group.

Katzin and Gebert (89) studied the absorption of lithium (I) chloride, lithium(I) nitrate, cobalt(II) chloride, and nickel(II) nitrate on anion resins in chloride and nitrate forms from acetone solution. They noted that the whole salt was retained and suggested as a plausible mechanism that the salts of the transition elements might be adsorbed as complex anions. On the other hand, Davies and Owen (86) have postulated the possibility of the passage of the salts from acetone solutions into the resin by a solvent extraction process. Tuck and Welch (90) reported the adsorption of plutonium(IV) onto strong anion resin from nitric acid-diethyleneglycoldibutyl ether solution as the result of the formation of anion complexes. Lofberg (91) studied the adsorption of antimony(III) chloride and bromide and indium(III) chloride and bromide on both anion and cation exchange resins. The solvent in these studies was anhydrous acetic acid containing alkali halides or potassium(I) acetate. It was suggested that the adsorption from these solvent mixtures took place through molecular reactions rather than through ionic reactions.

A number of separations on ion exchange resins using a nonaqueous or mixed solvent eluting agent have recently appeared in the literature. Venturello et al. (92) separated the alkali metals chromatographically on a cation exchange resin. The eluting agent was a mixture of 25 g. of phenol, 50 ml.

of methyl alcohol, and 25 ml. of water. The separation of lithium(I) and sodium(I) is complete while a slight overlap occurs in the sodium(I)-potassium(I) separation. The eluting agent was the same as that used by Magee and Headridge (93) for the paper chromatographic separation of the alkali metals. Davies and Owen (86) also separated the alkali metals on a strong cation resin. The eluting agent was 80 percent acetone, 20 percent water, and 0.7 M hydrochloric acid. A partial separation of the isotopes of lithium was also obtained by the same method.

Kember _et al_. (94) separated copper(II) and nickel(II) on a strong cation resin using an acetone or isopropyl alcohol solvent containing 4 percent hydrochloric acid and 10 percent water, by volume. In the presence of small amounts of water copper(II) could easily be eluted while if an anhydrous system was used elution was much slower. However, more than 20 percent water in the solvent caused a decrease in its eluting power. Elution characteristics of several other transtion metal ions were also reported. Similarly, zinc(II) and copper (II) were separated by Buznea _et al_. (95). These investigators used an acetone eluting agent containing 0.5 percent hydrochloric acid and 20 percent water.

Ziegler (96) used a precipitation technique for the retention of lead(II) on a strong base type resin in the sulfate form. The resin will retain the lead(II), presumably as lead

(II) sulfate, quantitatively only if the solvent contains 50 percent methyl alcohol, ethyl alcohol, or isopropyl alcohol. Similarly, lead(II), mercury(II), and copper(II) are retained quantitatively by an iodide form resin.

Two interesting applications of non-aqueous media in ion exchange were reported by Sansoni (97) and Brusset and Kikindai (98, 99). Sansoni used molten urea as the solvent for the separation of cobalt(II) and nickel(II). More than 96 percent of the cobalt(II) and less than 5 percent of the nickel(II) was retained by a strong anion resin. The latter workers removed positively charged iodine or bromine from compounds such as iodine nitrate, bromine nitrate, and iodine by a hydrogen form ion exchange resin. Absolute ethyl alcohol was the solvent used. These could then be transformed into sulfates by exchange of cations.

Iguchi separated a series of sulfur anions (sulfate, sulfite, thiosulfate, and sulfide) (100) and a mixture of tellurite, selenite, and sulfite (101) on a strongly basic type resin. In both cases, a neutral sodium(I) nitrate or an ammonium(I) nitrate solution can be used as the eluting solution. The effect of organic solvents in the eluting agent was studied by measurement of adsorbabilities. The addition of ethyl alcohol or acetone to the neutral eluting agent caused an increase in adsorbability of all anions except tellurite and selenite which remain the same.

Methyl n-propyl ketone plus a varying percent of water and molarity of hydrochloric acid was the eluting agent used by Carleson (102) for separations on a strongly acidic hydrogen form resin. Bismuth(III), cadmium(II), zinc(II), copper (II), cobalt(II) came off the resin in this order upon elution with the ketone containing 2 percent 10 M hydrochloric acid. Manganese(II) and cobalt(II) were then eluted by increasing the hydrochloric acid concentration to 15 percent 8 M and 30 percent 8 M, respectively. Finally, barium(II) was eluted with aqueous 8 M hydrochloric acid.

Burstall *et al*. (103) recovered gold(III) from cyanide liquor by adsorbing the heavy metal cyanides on a strong anion resin. After preliminary elutions to remove other metals the gold was eluted with an acetone solution containing 5 percent hydrochloric acid and 5 percent water or a nitric acid, water, and ethyl acetate solution of the same composition.

Korkisch used this enhanced adsorbability principle to retain thorium(IV) (104) on a strong anion resin in the nitrate form while other metals were being eluted with a mixture of nitric acid and water in ethyl alcohol. Similarly, uranium (VI) was separated from other metal ions (105) using hydrochloric acid and water in ethyl alcohol on a chloride form resin. Zinc(II) and cadmium(II) were separated chromatographically (strongly basic type resin in the chloride form) by Berg and Truemper (106) with an eluting agent containing 0.01

M hydrochloric acid and 10 percent methyl alcohol. If the methyl alcohol concentration is increased to 25 percent the column length could be reduced considerably and an effective separation is still possible.

Kojima (107, 108) and Yoshino and Kurimura (109) have studied adsorbabilities of several of the transition elements in mixed solvents containing hydrochloric acid on a strongly basic ion exchange resin in the chloride form. Two approaches were investigated. One was to hold the acid concentration constant and vary the percent of organic solvent. The other was to hold the percent of organic solvent constant and vary the hydrochloric acid concentration. Methyl alcohol, ethyl alcohol, n-propyl alcohol, and acetone were the organic solvents used. The measurement of distribution coefficients in various acid, water, solvent combinations were compared to those found in water-acid mixtures by Kraus (39, 40). In all cases, a significant increase in adsorption occurred which was dependent upon the acid concentration and percent of organic solvent, as well as type of solvent, present. If the acid concentration is held constant and the percent of organic solvent is increased, the adsorbability increases. Similarly, if the two are reversed an increase also occurs. The order of the increase, was found to be acetone $\geq$ ethyl alcohol $>$ methyl alcohol $>$ n-propyl alcohol. The distribution data were used to predict eluting conditions for a few metal ion mixtures and were illustrated by elution curves. The eluting scheme was applied to the analysis of aluminum(III) and copper(II) in die-cast zinc alloys. It was suggested that these solvent effects may be, as a first approximation, explained by the increase in the formation of negatively charged chloro-complexes of the metal ions. A decrease in the tendency for solvation of the metal ions in mixed solvents would promote this increase in complex formation.

Of manifest importance to the investigation to be described herein is the work of Kraus (39, 40) and the work discussed in the previous paragraph. Their basic methods have been broadened by alteration of the hydrochloric acid eluting scheme. This was done by replacing part of the water in the eluting agent with an organic solvent. Methyl alcohol, ethyl alcohol, isopropyl alcohol, acetone, and dioxane and combinations of these were the solvents used. Enhancement of adsorbability occurs and this advantage is used for metal ion separations. The quality of some separations, and, of more importance, the number of possible separations has been increased by conducting a systematic distribution coefficient study.

# EXPERIMENTAL

## Apparatus

Glassware: Kimble "nomax" burettes and Kimble "exax" pipettes were used throughout this work. Ground glass stoppered 125 ml Erlenmeyer flasks were used in the determination of the distribution coefficients. All other volumetric glassware used was class A. Ion exchange columns used for the separations are illustrated in Figure 1. The length of the column is such that there is at least 4 cm. of void space between the top of the resin bed and top of the glass column. The coarse glass frit supports the resin while still permitting a rapid flow rate. A long stem funnel serves as the reservoir. The inside diameter of the columns used were 1.1 and 2.2 cm. respectively.

pH Meter: All pH measurements were made with a Beckman Model G pH meter equipped with Beckman 1190-80 glass and 1170 calomel reference electrodes.

Spectrophotometer: A Beckman Model B spectrophotometer with one cm. borosilicate glass cells was used for conventional spectrophotometric measurements. The modified Model B (110) was used for spectrophotmetric titrations. A Cary Model 14 (1.0 cm. cells) was used for wavelength scanning.

Stirrer: A Burrell shaker was used for the equilibration studies.

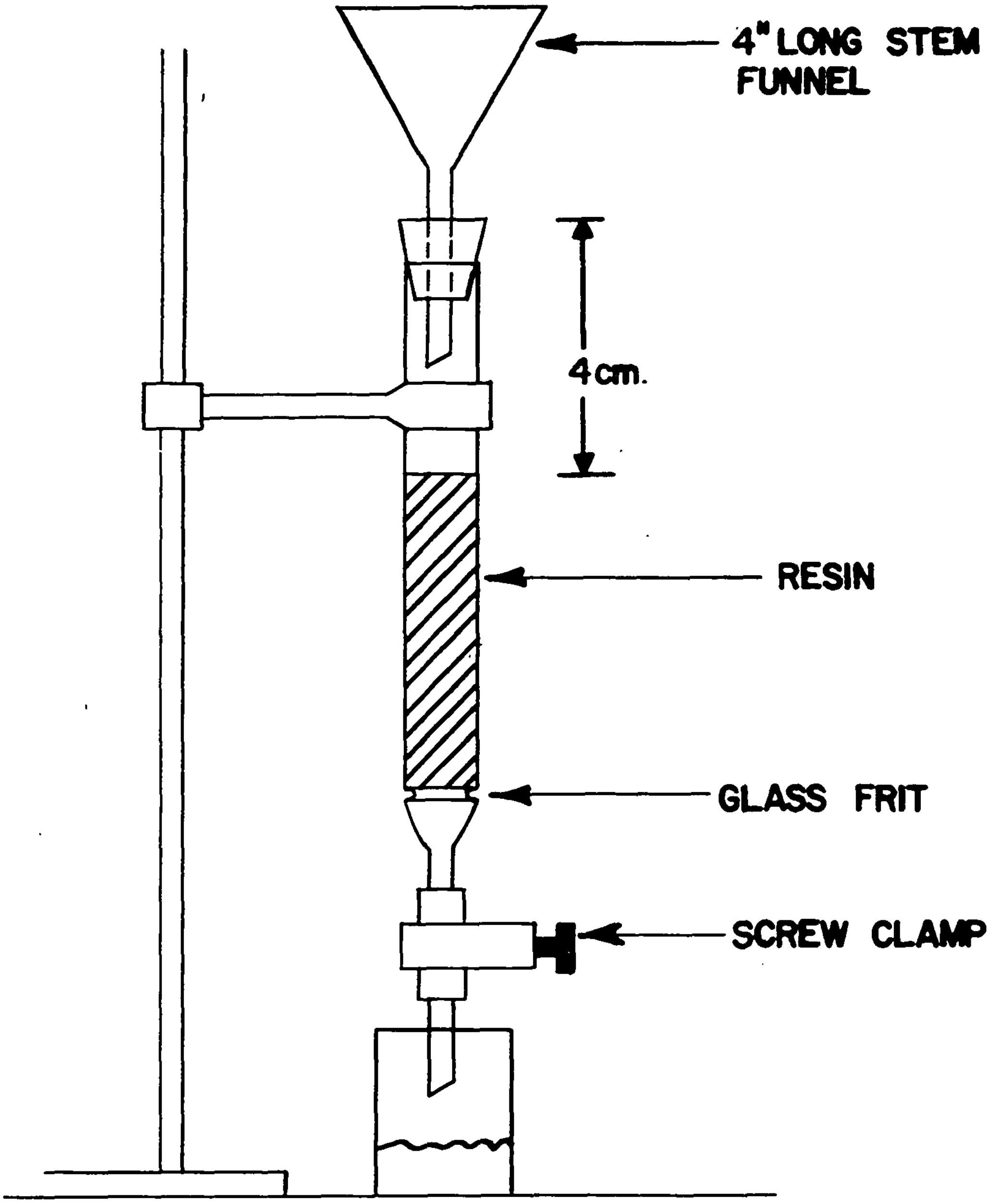

Figure 1. Ion exchange column

## Reagents

Ion Exchange Resin: J. T. Baker Chemical Company "Analyzed Reagent" Dowex 1 x 8 was the resin used in this study. Two mesh sizes, 100 to 200 and 200 to 400 mesh, of this strongly basic ion exchange resin were used. Regeneration of the resin for continual use was done by the following procedure: The resin (about 2 pounds) was first backwashed with 2 to 2.5 M perchloric acid until the effluent gives a negative chloride test. An additional liter of the perchloric acid solution was passed through the column (about 4 liters total). Conversion of the resin to the perchlorate form will remove any metallic impurities which might be present. After washing the resin with water to remove the excess perchloric acid the resin was converted to the chloride form by passage of 4-6 liters of 2-2.5M hydrochloric acid. This was followed by elution with 2 liters of 1 M and then 2 liters of 0.005 M hydrochloric acid. The excess acid was rinsed away with water and the resin was filtered with suction. The excess water was removed by washing with absolute ethyl alcohol and then acetone. The chloride form resin was air dried and had a water content of about 5 to 10 percent by weight.

EDTA [disodium dihydrogen (ethylenedinitrilo) tetraacetate dihydrate] : Eastman Chemical Company white label grade.

Zinc Metal: Primary standard zinc metal of 99.99 percent purity obtained from the Platt Brothers and Company, Waterbury, Connecticut.

Metal Ions Investigated: Rare earth(III) and scandium (III) oxides were obtained from the Ames Laboratory of the United States Energy Commission. All others were reagent grade chloride salts except vanadium(IV), uranium(VI), and thorium(IV). Vanadium was used as the sulfate ($VOSO_4$). Uranyl acetate and thorium nitrate were converted to the chlorides by anion exchange with chloride form resin. The metal perchlorates used were from the G. F. Smith Chemical Company.

Organic Solvents: J. T. Baker purified methyl alcohol, absolute ethyl alcohol, Fisher certified isopropyl alcohol, Mallenckrodt analytical grade acetone, and Fisher purified dioxane were the solvents used.

Organic Solvent-Water-Hydrochloric Acid Mixtures: The mixtures were made so that the concentration of organic solvent and water were expressed as percent by volume and the hydrochloric acid concentration as molarity (M). For example, if one liter of an 80 percent isopropyl alcohol-1 M hydrochloric acid mixture was needed, it was prepared as follows: Eight hundred ml. of isopropyl alcohol, 83 ml. of concentrated hydrochloric acid, and 117 ml. water were mixed together. Any changes in volume due to mixing were disregarded.

Metal Chloride or Perchlorate Solutions: The chloride or perchlorate salts were dissolved in water with a sufficient amount of either hydrochloric or perchloric acid present to prevent hydrolysis and diluted to volume. The oxides were dissolved by the appropriate acid (small excess) and diluted to volume. In some cases the solutions were prepared to contain a known percent of organic solvent or concentration of hydrochloric acid. All of these solutions were then standardized by an appropriate method. A more detailed description as to exact concentrations of the two previous stock solutions will be found in a later section.

Metal Chloride Solutions for Separations: Stock solutions containing about 1.8 mg. of metal ion/ml. (exact concentration determined) were prepared from the metal chloride or oxide. Similarly, stock solutions containing 18 mg. metal ion/ml. were prepared.

All other chemicals except indicators and colorimetric reagents were common reagent grade laboratory chemicals. See references for information on specific indicators and colorimetric reagents used in analysis. Also, whenever the word water is used distilled, deionized water is implied unless otherwise stated.

## Analytical Procedures

### A. Titration methods

EDTA: Solutions of EDTA were standardized against standard zinc(II) solution using azoxine indicator as described by Fritz *et al*. (111). Standard zinc(II) solution was prepared by weighing an appropriate amount of pure zinc metal.

Cadium(II), Zinc(II), Copper(II), and Cobalt(II): These metal ions were determined by an EDTA titration method using azoxine indicator (111).

Iron(III): Analyses of iron(III) samples were performed by an oxidation-reduction method. The sample in dilute hydrochloric acid was passed through a lead reductor. This was followed by a one percent hydrochloric acid wash solution. The effluent containing iron(II) was titrated with standard cerium(IV) (in sulfuric acid) using ferroin as indicator (112).

Rare Earths(III) and Thorium(IV): These ions were analyzed by an EDTA titration method using arsenazo indicator (113). A modification in the thorium(IV) procedure was employed. The titration was performed at 80° C or higher.

Scandium(III): Analysis was by EDTA titration with methylthymol blue as indicator. This was also titrated at temperatures of 80° C or higher.

Manganese(II): Analysis was by EDTA titration with Eriochrome Black T as indicator. The titration was performed at 80° C in the presence of ascorbic acid (114).

Uranium(VI): Analysis was by the oxidation-reduction method of Sill and Peterson (115).

Zirconium(IV): Analysis was by the back titration EDTA method, using thiourea indicator, of Fritz and Johnson (116).

Bismuth(III): Analysis was by an EDTA titration using thiourea indicator (117).

Chromium(III): Chromium(III) was analyzed by an oxidation-reduction method. Oxidation of chromium(III) to chromium(VI) was done by adding hydrogen peroxide (30 percent) to the basic (NaOH) solution. All of the excess peroxide was removed by heating the solution. The solution was then acidified with sulfuric acid up to 4 M and titrated with standard iron (II) solution using ferroin indicator.

Vanadium(IV): Ascorbic acid was first added to the solution to prevent oxidation of the vanadium(IV). This was followed by the addition of a measured excess of standard EDTA. The excess, after a ten minute reaction period, was titrated with a standard zinc solution using azoxine as indicator.

Calcium(II): Analysis was by EDTA titration with thymolphthalexone as indicator (118).

Magnesium(II): Analysis was by EDTA titration using Eriochrome Black T as indicator (114).

## B. Colorimetric methods

Copper(II), Zinc(II), Thorium(IV), Uranium(VI), Bismuth (III), and Iron(III): The colorimetric reagent used for the analysis of copper(II) solutions was neocuproine (119). The procedure was modified by making the solution 50 percent isopropyl alcohol by volume. Zinc(II) (120) was determined by the reagent zincon. Thorin (121) was used for the determination of thorium(IV) while arsenazo (122) was used for uranium(VI). Thiourea (123) and 1, 10 phenanthroline (112) were used for bismuth(III) and iron(III), respectively.

### Measurement of Distribution Coefficients

There are two approaches to the development of separation procedures by ion exchange. One is a trial and error process while the other is to determine adsorbabilities (distribution coefficients) over a wide range of conditions. The latter approach is more fruitful because optimum media for adsorption and elution can be established more readily from these data. Measurement of the distribution coefficients can be done by either a batch method or one of several column methods.

All distribution coefficients reported here were measured by the batch method using Dowex 1 X8, chloride form, 100 to 200 mesh resin. It was felt that the advantages of the batch method, simultaneous equilibration of a large number of samples, ease in analysis, and relatively short time per experiment, outweighed the advantages of the column methods. The batch method consists, simply, of equilibrating small known amounts of resin and solution, followed by analysis of one or both of the phases. In all of these studies the aqueous phase was analyzed before and after equilibration. The concentration of metal ion on the resin was determined by difference.

The distribution coefficients may be expressed in any convenient set of units. Amount of metal per gram of dry resin and amount of metal per milliliter of solution were the units chosen. The batch distribution coefficient, D, was then computed according to equation 4:

$$D = \frac{\text{meq. metal on resin/g. of dry resin}}{\text{meq. metal in solution/ ml. of solution}} \qquad (4)$$

The batch-distribution coefficient, D, is related to the volume distribution coefficient $D_v$, from column methods, by the following equation:

$$D_v = D\rho \qquad (5)$$

where $\rho$ is the bed density (kg. of dry resin per liter of bed). $\rho$ is determined by measuring the volume of a settled wet column containing a known weight of dry exchanger. $D_v$ in turn, can be related to the volume of eluent required to elute the constituent to its adsorption or elution maximium on the Gaussian elution curve by the following equation:

$$D_v = \frac{v}{Ad} - i \qquad (6)$$

Here, 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.

The dry weight of the resin was calculated from the air-dried weight and the moisture content of the resin. The moisture content of the resin was determined by drying a weighed amount of the air-dried resin in an oven at 90-100° C. The resin was then placed under a vacuum for four to six hours. From the loss in weight, which reached a minimum after two dryings, the moisture content was calculated. This was determined each time a series of equilibration studies were carried out. The moisture content ranged from 5 to 10 percent by weight.

Knowledge of the time needed to reach equilibrium was required before the distribution coefficients could be accurately determined. It is known that equilibrium is reached at a slower rate in a mixed or nonaqueous solvent than in water. This information is also helpful in determining optimum flow rates in column operations. Equilibration time was measured by determining the distribution coefficients, as described later, of copper(II) chloride in 18, 37, 55, and 74 percent isopropyl alcohol-1 M hydrochloric acid vs. time. The times at which the distribution coefficients reached a maximum were $< 10$, $< 10$, 10, and 30 minutes, respectively. To insure equilibrium was reached, particularly when the mixture was above 80 percent organic by volume, more than ample time was allowed in the distribution coefficient determinations.

The distribution coefficient should be independent of the absolute solute concentration. In order to meet this requirement the solute should occupy approximately 3 percent of the resin capacity or less. The capacity of the resin used in this work was known to be about 3.8 meq./g. However, the exact adsorbing species is not known and this prevents calculation of the proper concentration of metal ion to use in the equilibration. To determine this concentration the distribution coefficients of several metals [copper(II), manganese(II), and nickel(II) chloride] were measured as a function of the metal ion concentration while holding the solvent composition constant. Figure 2 illustrates the variance of copper ion in 90 percent ethyl alcohol-0.3 M hydrochloric acid and nickel ion in 90 percent isopropyl alcohol-0.3 M hydrochloric acid. Any concentration on the horizontal part of the curve can be used. To further minimize any changes in the distribution coefficients, approximately the same metal ion concentration was used in all the determinations except in the constant hydrochloric acid-varying ethyl alcohol and constant acid and water-mixed organic solvent studies. The concentration used was 0.007 M ± 0.0005 in the former and 0.0042 M ± 0.0004 in the latter two.

A detailed procedure used for the distribution coefficient measurement is as follows: Approximately 1 gram of air-dried resin is accurately weighed into a 125 ml. ground glass stoppered Erlenmeyer flask. Fifty ml. of the appropriate organic solvent-water-hydrochloric acid mixture and 4 ml. of the metal ion solution are then pipetted into the flask. The flask is stoppered and shaken on the Burrell shaker for 12 to 18 hours for organic solutions of 80 percent or less and 22 to 32 hours for those above 80 percent. (The temperature in this work was 24 ± 1° C.) After the equilibration period an aliquot of the liquid phase is removed. The excess acid and organic solvent are evaporated by mild heating and the analysis is completed by either a titrimetric or colorimetric method, depending upon

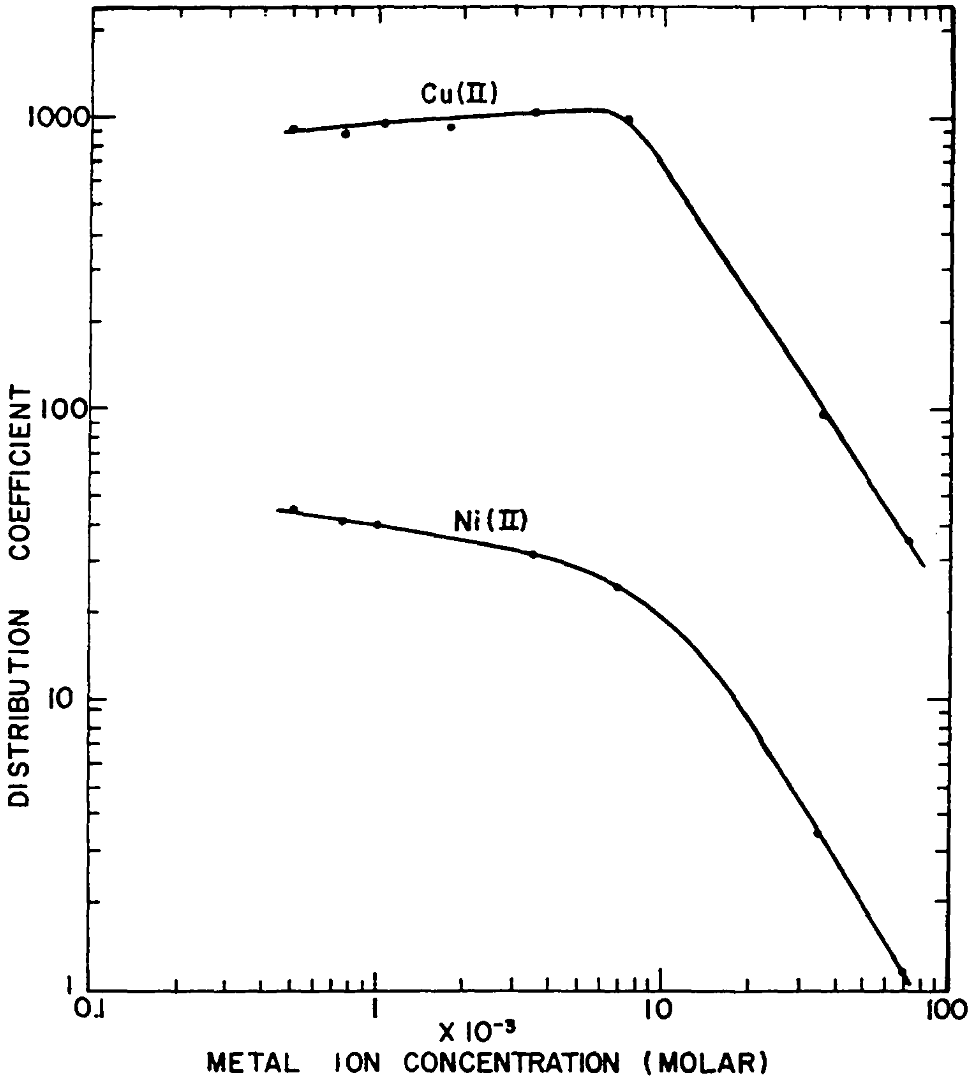

Figure 2. Distribution coefficients of nickel(II) chloride in 90 percent isopropyl alcohol-0.3 M hydrochloric acid and copper(II) chloride in 90 percent ethyl alcohol-0.3 M hydrochloric acid vs. metal ion concentration

the concentration of the metal ion present. Since the composition of both the solvent and metal ion solution are known, the concentration of the various components in contact with the resin are then calculated assuming changes in volume due to mixing are negligible.

## Preparation of Columns

A slurry of the resin, Dowex 1 X8, chloride form, 200 to 400 mesh, in 95 percent ethyl alcohol-0.3 M hydrochloric acid is prepared and stirred to equilibrate the resin with the solvent mixture. The slurry is then poured into the glass column which contains 5-10 ml. of the alcohol-acid mixture until the desired height is reached. The liquid level is adjusted to be 1.5 to 2 cm. above the resin bed. Approximately 50 ml. of the acid-alcohol mixture is then passed through the column at a moderate flow rate. In this manner complete settling of the resin column is obtained. Also, the void space and solvent uptake of the resin is of the same composition as the eluting agent. Elution is continued until the liquid level is about 1/16 of an inch above the resin. The tip of the funnel is lowered to about one cm. above the resin bed. At this point the metal mixture, using either of the sampling techniques described in the next section, is slowly transferred to the funnel reservoir. After rinsing the sample into the resin column with the 95 percent alcohol-acid mixture and adjusting the liquid level to about 1/16 of an inch above the resin bed, a small portion of the eluting agent is added. The tip of the funnel is raised to about 2 cm. above the resin bed and the remaining eluting agent is added slowly so as not to disturb the resin. When the elution of the first metal is complete the level is adjusted to about 1/16 of an inch above the resin bed and the second eluting agent is slowly added. Subsequent elutions are treated similarly.

## Sampling Technique

Two sampling techniques were employed in the separation studies. The first technique involved pipetting of an ethyl alcohol-hydrochloric acid-metal chloride mixture. The mixture was prepared by taking 10 ml. aliquots from solutions containing 18 mg. of metal ion/ml. (chloride solution) and evaporating the water mixture in a small beaker to near dryness at a slow rate. The residue was then dissolved in 2.5 ml. of concentrated hydrochloric acid and 2.5 ml. of water. This was transferred to a 100 ml. volumetric flask. The beaker was rinsed with absolute ethyl alcohol and this was added to the flask. The mixture was diluted to volume with absolute ethyl alcohol. This gave a solution of 0.3 M hydrochloric acid, 1.8 mg. of each metal ion/ml., and approximately 95-96 percent ethyl alcohol. Suitable aliquots of this mixture were then transferred to the ion exchange column. Similar solutions were prepared of each metal ion and standardized. This technique was employed only in 1:1, by weight, metal ion concentrations. It is, however, adaptable to different ratios. A disadvantage of this method is that volumetric errors may be encountered. This is possible because the volumetric glassware is calibrated for water solutions and not alcoholic solutions.

The second technique avoided pipetting of alcohol solutions. The metal ion mixture was prepared by taking suitable aliquots of the standardized 1.8 mg. metal ion/ml. chloride solutions and transferring them to a beaker. The solution was evaporated to near dryness at a slow rate. Five ml. of a 96 percent ethyl alcohol-0.3 M hydrochloric acid mixture was added. After the residue dissolved, 5-10 minutes, the resulting solution was transferred to the ion exchange column. The beaker was rinsed with a solution of 95 percent ethyl alcohol-0.3 M hydrochloric acid and this was also transferred to the column. A disadvantage of this technique is the necessity of rinsing the beaker thoroughly after transferring the sample. The tenacity of the alcoholic solution to the glass requires complete and careful rinsing so that excessive volumes of wash solution are not used. Also, in some cases, the residue will dissolve very slowly. This latter technique was used in the major portion of the separations reported here.

## DISCUSSION OF DISTRIBUTION COEFFICIENT DATA

The batch distribution coefficient can be altered by changing the composition of the solvent in three ways. In general, as the concentration of the hydrochloric acid is increased the distribution coefficient increases. Similarly, as the percent of organic solvent is increased the distribution coefficient increases. The third method is to change the organic solvent. By taking advantage of these three routes a systematic approach to the distribution coefficient study was initiated with the ultimate goal being the application of these data to separations.

Distribution coefficients for copper(II) chloride in 28, 37, 55, 65, 74, 90, and 95 percent isopropyl alcohol with varing hydrochloric acid concentration are given in Table 1 and plotted in Figure 3. This family of curves illustrates the increase in distribution coefficient as the hydrochloric acid concentration or isopropyl alcohol concentration is increased. It is interesting to note that in aqueous solution copper(II) is retained by the resin beginning at about 2 M hydrochloric acid and reaches a maximum at about 6 M, $D_v = 1$, $D = 2.2$ and $D_v = 10$, $D = 22$, respectively (39). Particularly striking is the comparison of these values to those found in 90 and 95 percent isopropyl alcohol-0.01 to 0.2 M hydrochloric acid. This respective D range, 280-770 and 79,000-87,000, is also striking in that an increase by a factor of about 100 occurs with a 5 percent increase in isopropyl alcohol.

Distribution coefficients were measured for a series of metal chlorides in 95, 90, 74, 65, and 55 percent isopropyl alcohol at varying concentrations of hydrochloric acid. The distribution coefficients measured for cobalt(II), manganese (II), nickel(II), and calcium(II) chlorides in 95 and 90 percent isopropyl alcohol-0.01 to 0.2 M hydrochloric acid are given in Table 2 and Table 3 and plotted vs. hydrochloric acid concentration in Figure 4 and 5, respectively. The values found for uranyl(VI), cobalt(II), thorium(IV), dysprosium(III), calcium(II), and nickel(II) chlorides in 74 percent isopropyl alcohol at varying concentrations of hydrochloric acid are given in Table 4 and plotted vs. the acid concentration in Figure 6. Similarly, Table 5 and Figure 7 contains the distribution coefficient values found for cobalt(II), calcium(II), nickel(II), and thorium(IV) chlorides in 65 percent isopropyl alcohol with varying hydrochloric acid concentrations. Table 6 and 7 respectively, contains the data found for bismuth(III), cadmium(II), zinc(II), uranyl(VI), iron(III), cobalt(II), and manganese(II) chlorides (strongly adsorbed group) and chromium (III), vanadyl(IV), (sulfate), lanthanum(III), thorium(IV), calcium(II), nickel(II) and zirconium(IV) chlorides (weakly adsorbed group) in 55 percent isopropyl alcohol at varying hydrochloric acid concentrations. These are plotted in Figure 8 (strongly adsorbed group) and in Figure 9 (weakly adsorbed group). Data previously presented for copper(II) chloride, Table 1 and Figure 3, are also included in these graphs for comparison purposes.

The distribution curves of the strongly adsorbed metals (cobalt(II) and higher), except those in 90 and 95 percent isopropyl alcohol (Figure 4 and 5), are very similar in shape to those found by Kraus in aqueous hydrochloric acid (39). The principal difference is the enhanced adsorption or retention at lower acid concentrations which is dependent on the amount of organic solvent present. Considerable differences occur in the case of the weakly adsorbed group. In aqueous hydrochloric acid, calcium(II), nickel(II), thorium(IV), and rare earths (III) exhibit no adsorption even when the acid concentration is as high as 12 M. In 95 percent isopropyl alcohol-0.2 M hydrochloric acid the D values for nickel(II) and calcium(II) are about 100 and 60, while in 90 percent isopropyl alcohol-0.2 M hydrochloric acid the values drop to 45 and 31, respectively. Significant retention also occurs in 74, 65, and 55 percent isopropyl alcohol, but to a lesser extent. Thorium (IV) and rare earths(III) also show significant retention having D values of 17 and 10 at 2.4 M hydrochloric acid-74 percent isopropyl alcohol. Manganese(II), chromium(III), and vanadyl (IV) exhibit different properties in 55 percent isopropyl alcohol than in aqueous hydrochloric acid. In the latter solution manganese(II) starts to show slight adsorption at about 7-8 M acid and reaches a maximum D value of about 5 at approximately

10 M hydrochloric acid. In the alcoholic-acid solution the D value reaches a maximum of 27 at 4.5 M hydrochloric acid and is still increasing. (Maximum points were not reached in several instances because the volume requirements of the mixtures prevented further addition of concentrated hydrochloric acid. However, higher concentrations could probably be attained by dissolving gaseous hydrogen chloride in the mixture.) Chromium(III) and vanadyl(IV) are classified in the slight adsorption group by Kraus (39), i.e., in 12 M hydrochloric acid 0.6 $\leq$ D $\leq$ 2.2. In the 55 percent isopropyl alcoholic-acid mixture slight retention by the resin starts to occur at about 1.5 M acid and reaches D values of about 4 and 6, respectively. Of the metals studied only zirconium(IV) shows less adsorption in the alcoholic medium. However, the adsorption that does occur starts at a lower hydrochloric acid concentration, 2 M vs. 7 M in water. Maximum adsorption for zirconium(IV) (see Figure 9) could not be determined because of its hydrolytic or solubility properties, with precipitation occurring at 3.5 M hydrochloric acid.

Distribution coefficient data are given in Table 8 and plotted in Figure 10 for the solvent system 96 percent isopropyl alcohol-0.0005 to 0.01 M hydrochloric acid for copper (II), cobalt(II), nickel(II), manganese(II), and calcium(II) ions. The perchlorate salts were used so that the only chloride present would be that associated with the resin and the chloride from the hydrochloric acid in the solvent. It will be noticed that the retention falls slowly, implying that no chloride ion in the form of hydrochloric acid need be present. However, the presence of perchlorate anion affects the retention as seen by the comparison of Figure 10 and Figure 5. This decrease by a factor of about 10 is due to the greater affinity which the resin has for the perchlorate anion and probably follows the desorption process illustrated in the following equation:

$$RCl \cdot MCl_n + ClO_4^- \rightleftharpoons RClO_4 + \left[Cl^- + MCl_n\right] \qquad (7)$$

R = Resin

In this reaction the metal being retained either by ion pair formation or as a negatively charged chloro-complex is displaced by the perchlorate anion yielding the ion pair and chloride anion or a negatively charged chloro-complex (50).

The perchlorate desorption effect was further illustrated by the determination of the distribution coefficients for the same metals [copper(II), cobalt(II), nickel(II), manganese(II), and calcium(II)] as perchlorate salts in 97 percent isopropyl alcohol-0.02 to 0.2 M perchloric acid. These data are given in Table 9 and plotted in Figure 11. The only chloride present is that associated with the resin. If a complete perchlorate system is used no adsorption occurs. This was found when copper (II), manganese(II), and nickel(II) perchlorate were equilibrated with perchlorate form resin in 95 percent isopropyl alcohol-0.05 to 0.2 M perchloric acid.

The effect of the type of organic solvent was determined. Table 10 contains the D values found for copper(II) chloride in 74 percent ethyl alcohol, -acetone, -dioxane, and -ethylene glycol with varying hydrochloric acid concentration. Table 11 contains the data found for constant 1 M hydrochloric acid with varying percent of organic solvent. The data are plotted in Figure 12a and 12b, respectively. The previously graphed data for copper(II) in isopropyl alcohol (see Table 1 and Figure 3) are also included for comparison. Enhanced adsorption in Figure 12b follows the order: dioxane > acetone > isopropyl alcohol = ethyl alcohol. The order of the dielectric constants of the solvents is: ethyl alcohol > acetone > isopropyl alcohol $\gg$ dioxane (124). Simple correlations with the dielectric constant are not readily apparent. This is probably due to the different solvation properties of the solvents and the necessity of considering the effect of hydrochloric acid and water on the dielectric constant. In addition, the values obtained in 1 M hydrochloric acid-74 percent acetone or dioxane as well as higher concentrations of the acid are not very accurate. Condensation reactions in the acetone solutions and some immiscibility in the dioxane solutions were apparent.

To illustrate further the effects of the type of solvent, distribution coefficients in 96 percent methyl alcohol, -ethyl alcohol, -isopropyl alcohol, -acetone, and -dioxane at 0.01 to 0.2 M hydrochloric acid for copper(II), cobalt(II), manganese (II), calcium(II), and nickel(II) as perchlorate salts were determined and are summarized in Table 12. The distribution coefficients are plotted against hydrochloric acid concentration in Figures 13 to 22. Figures 13 to 17 contain the curves found for the metal ions in each solvent while Figures 18 to 22 contain the different solvent curves for each metal ion. The high retention that the resin exhibits for calcium(II), nickel(II), and manganese(II) suggests adsorption of ion pairs or of undissociated molecules. This would be promoted in the solvents of lower dielectric constant. (In general, the ionizing power of a solvent is higher for the one having a higher dielectric constant.) However, evidence of chloro-complexes of the three metal ions have been reported (125). These in general are very weak and are probably mono-chloro-complexes. This would tend to imply that by addition of a solvent of low polarity, neutral molecules or ion pairs would be the dominant species. In the case of copper(II) and cobalt(II), the major species are probably negatively charged chloro-complexes. This is easily seen by the sharp color changes that occur upon addition of an organic solvent to a chloride solution of the metal ions. (The copper(II) solution turns to a yellow-brown color and the cobalt(II) solution to a brilliant blue color.) Comparison of absorption spectra illustrates this. In Figure 23 the absorption spectra of cobalt(II) is given for the conditions: aqueous-increasing hydrochloric acid concentration and constant hydrochloric acid concentration-increasing percent ethyl alcohol.

The strengths of several of the transition metal chloro-complexes have been measured in mixed solvents containing chloride ions (125). In general, these show enhancement in complex strength over that found in aqueous chloride solutions. The presence of the organic solvent appears to favor the dehydration of the aquated metal ions and consequently favors the formation of negatively charged complexes. This is conviently expressed by the following reactions for copper(II):

$$Cu(H_2O)_4^{+2} + Cl^- \rightleftharpoons CuCl(H_2O)_3^{+1} + H_2O \qquad (8)$$

$$CuCl(H_2O)_3^{+1} + Cl^- \rightleftharpoons CuCl_2(H_2O)_2^{\circ} + H_2O \qquad (9)$$

$$CuCl2(H2O)2^{\circ} + Cl \rightleftharpoons CuCl_3(H_2O)_1^{-1} + H_2O \qquad (10)$$

$$CuCl_3(H_2O)_1^{-1} + Cl^- \rightleftharpoons CuCl_4^{-2} + H_2O \qquad (11)$$

The adsorption of one of these species can take place. This can occur either by adsorption of negatively charged chloro-complexes [see reaction (12)] or by adsorption of a neutral complex or ion pair [see reaction (13)] .

$$n-2\ R\text{-}Cl + (CuCl_n)^{2-n} \rightleftharpoons R_{n-2}(CuCl_n)^{2-n} + n-2\ Cl^- \qquad (12)$$

R= Resin, n = 3 or 4.

$$R\text{-}Cl + CuCl_2 \rightleftharpoons R\text{-}Cl(CuCl_2) \qquad (13)$$

Furthermore the negatively charged chloro-complexes can react with the hydrogen ions [see reactions (14-16)] to form acidic chloro-complexes.

$$CuCl_3^- + H^+ \rightleftharpoons HCuCl_3 \qquad (14)$$

$$CuCl_4^= + H^+ \rightleftharpoons HCuCl_4^- \qquad (15)$$

$$HCuCl_4^- + H^+ \rightleftharpoons H_2CuCl_4 \qquad (16)$$

The dissociation of these acidic chloro-complexes would be controlled by the ionizing power and leveling effect of the organic solvent that is present. The adsorption of any of these acidic species could be similar to an extraction process. Many oxygenated solvents have been used for the extraction of metal chloro-complexes from hydrochloric acid solution (126). In this case, the uptake of the organic oxygenated solvent by the resin would serve as a stationary extracting agent.

To test the possibility of adsorption or extraction of the acidic species, solutions containing 0.005 M copper(II) chloride and 0.01 M hydrochloric acid in 95 percent methyl alcohol, ethyl alcohol, and isopropyl alcohol were passed continuously through columns of resin. The effluent was collected up to the copper(II) break through point and titrated with standard base. No significant decrease in acidity was found as would be indicated by the possible extraction or adsorption of the acidic copper chloro-complex. However, this does not rule out the extraction process. The mechanism of the process may be an initial extraction of a neutral species as illustrated in reaction (17).

$$\text{R-Cl(Solvent)} + \text{CuCl}_2 \rightleftharpoons \text{R-Cl(Solvent-CuCl}_2\text{)} \qquad (17)$$

A complexing reaction could then take place which would yield a product as illustrated in reaction (13). In the case of the non chloro-complexing metal ions, the process would stop with a product similar to that in reaction (17).

Unfortunately, the exact nature of the retained species is difficult to ascertain. This is readily apparent in light of the previous discussion and the contrary views of Katzin and

Gebert (89) and Davies and Owen (86) on adsorption in acetone solution. Undoubtedly, the dielectric constant which reflects many of a solvents properties is an important factor in the uptake of metal ions by the resin. However, a theory must be developed individually for each solvent because the properties are often specific for certain solvents.

The distribution coefficient curves in high percent ethyl alcohol with low hydrochloric acid concentration (see Figure 14) are similar to the aqueous hydrochloric acid curves in that calcium(II) and nickel(II) are only slightly retained. In contrast, manganese(II), cobalt(II), and copper(II) show enhanced retention. It appeared that an elution scheme could be based on changes in percent ethyl alcohol while holding the hydrochloric acid concentration constant. Distribution coefficients for cadmium(II), zinc(II), bismuth(III), uranyl(VI), iron(III), copper(II), cobalt(II), manganese(II), thorium(IV), dysprosium (III), lanthanum(III), vanadyl(IV) (sulfate), chromium(III), nickel(II), and calcium(II) chlorides in constant 0.3 M hydrochloric acid with varying percent of ethyl alcohol are given in Table 13 and 14, strongly adsorbed and weakly adsorbed metal ions, respectively. The values are plotted against percent ethyl alcohol in Figure 24 for the strongly adsorbed metal ions and in Figure 25 for the weakly adsorbed metal ions. As expected, the enhanced adsorption decreases with a decrease in the ethyl alcohol concentration.

Of particular interest is the high thorium(IV) and dysprosium(III) adsorption. It appeared that by a combination of methyl and ethyl alcohol intermediate adsorption might occur which would yield more ideal conditions for separations. A comparison of the distribution coefficients in 96 percent methyl alcohol and ethyl alcohol with 0.2 M hydrochloric acid for nickel(II) and manganese(II) (see Figure 13 and 14) seemed to bear this out. Distribution coefficients measured for calcium(II), nickel(II), dysprosium(III), thorium(III), and scandium(III) in 0.2 M hydrochloric acid with varying amounts of methyl and ethyl alcohol totaling 96 percent are given in Table 15 and plotted in Figure 26. Similar measurements were made in methyl and isopropyl alcohol mixtures. These data are found in Table 16 and plotted in Figure 27.

For the separation of several metals conditions should be selected such that the distribution coefficients of all but one element are high. The latter element should have a distribution coefficient in the neighborhood of unity. In this manner each element may be removed within a few column volumes in sharp bands. It is evident from Figures 8 and 9, 24 and 25, and 26 that separation of a large number of elements, either in groups or individually, is feasible by the use of anion exchange resins and hydrochloric acid in mixed solvents. The application of the distribution coefficient data to separations was the next step and is discussed in the following section.

Table 1. Distribution coefficients of copper(II) (chloride salt) in water, isopropyl alcohol, and hydrochloric acid mixtures

| (HCl) | Percent alcohol | | | | | | |
|---|---|---|---|---|---|---|---|
| M | 95 | 90 | 74 | 65 | 55 | 37 | 28 |
| 0.01 | 8,970 | 282 | | | | | |
| 0.035 | 8,090 | 353 | | | | | |
| 0.05 | | | 2.5 | | | | |
| 0.07 | 8,040 | 448 | | | | | |
| 0.1 | 8,370 | 530 | 6.4 | 0.6 | | | |
| 0.2 | 8,710 | 776 | | | | | |
| 0.5 | | | 23.3 | 6.4 | 1.2 | | |
| 1.0 | | | 63.0 | 18.8 | 5.7 | 0.8 | 0.3 |
| 1.5 | | | 131 | 37.1 | 13.9 | | |
| 2.0 | | | 224 | 66.3 | 27.5 | 5.7 | 2.4 |
| 2.4 | | | 257 | | | | |
| 2.5 | | | | 107 | 44.2 | | |
| 3.0 | | | | 135 | 76.8 | 17.4 | 7.9 |
| 3.5 | | | | 149 | 84.7 | | |
| 4.0 | | | | | 93.4 | 35.4 | 14.3 |
| 4.5 | | | | | 98.1 | | |
| 5.0 | | | | | | 47.3 | 31.7 |

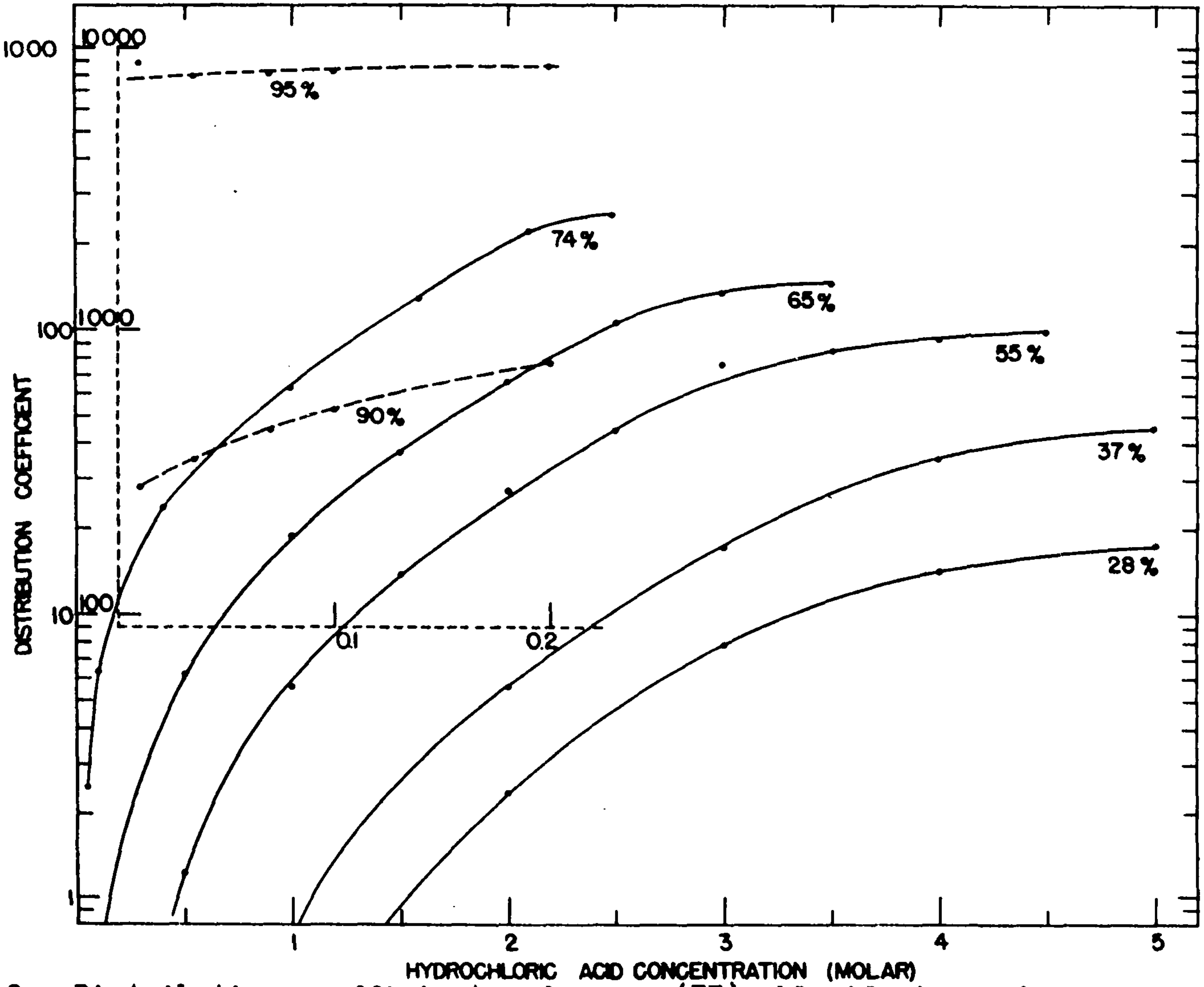

Figure 3. Distribution coefficients of copper(II) chloride in various concentrations of isopropyl alcohol vs. hydrochloric acid concentration

Table 2. Distribution coefficients of metal ions (chloride salts) in 95 percent isopropyl alcohol with varying hydrochloric acid concentration

| (HCl) | Metal ion | | | |
|---|---|---|---|---|
| M | Co(II) | Mn(II) | Ni(II) | Ca(II) |
| 0.01 | 7,140 | 897 | 55.5 | 88.4 |
| 0.035 | 8,320 | 1,230 | 61.1 | 100 |
| 0.07 | 10,100 | 974 | 66.3 | 99.2 |
| 0.1 | 12,600 | 1,370 | 66.4 | 112 |
| 0.2 | 10,100 | 2,520 | 63.6 | 109 |

Table 3. Distribution coefficients of metal ions (chloride salts) in 90 percent isopropyl alcohol with varying hydrochloric acid concentration

| (HCl) | Metal ion | | | |
|---|---|---|---|---|
| M | Co(II) | Mn(II) | Ni(II) | Ca(II) |
| 0.01 | 78.9 | 24.7 | 19.2 | 24.2 |
| 0.035 | 117 | 32.8 | 23.6 | 29.4 |
| 0.07 | 161 | 39.4 | 25.9 | 34.0 |
| 0.1 | 211 | 45.9 | 27.1 | 38.9 |
| 0.2 | 430 | 67.8 | 31.3 | 45.4 |

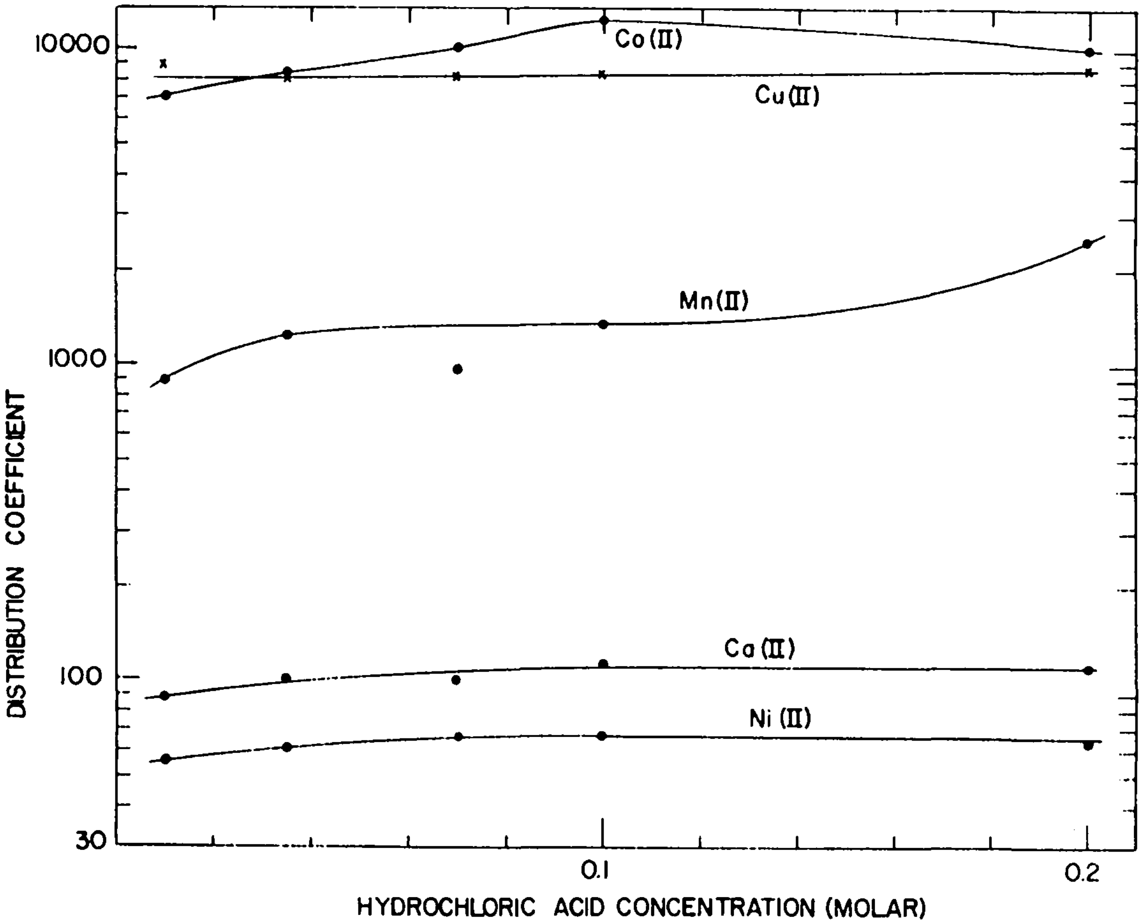

Figure 4. Distribution coefficients of metal chlorides in 95 percent isopropyl alcohol vs. hydrochloric acid concentration

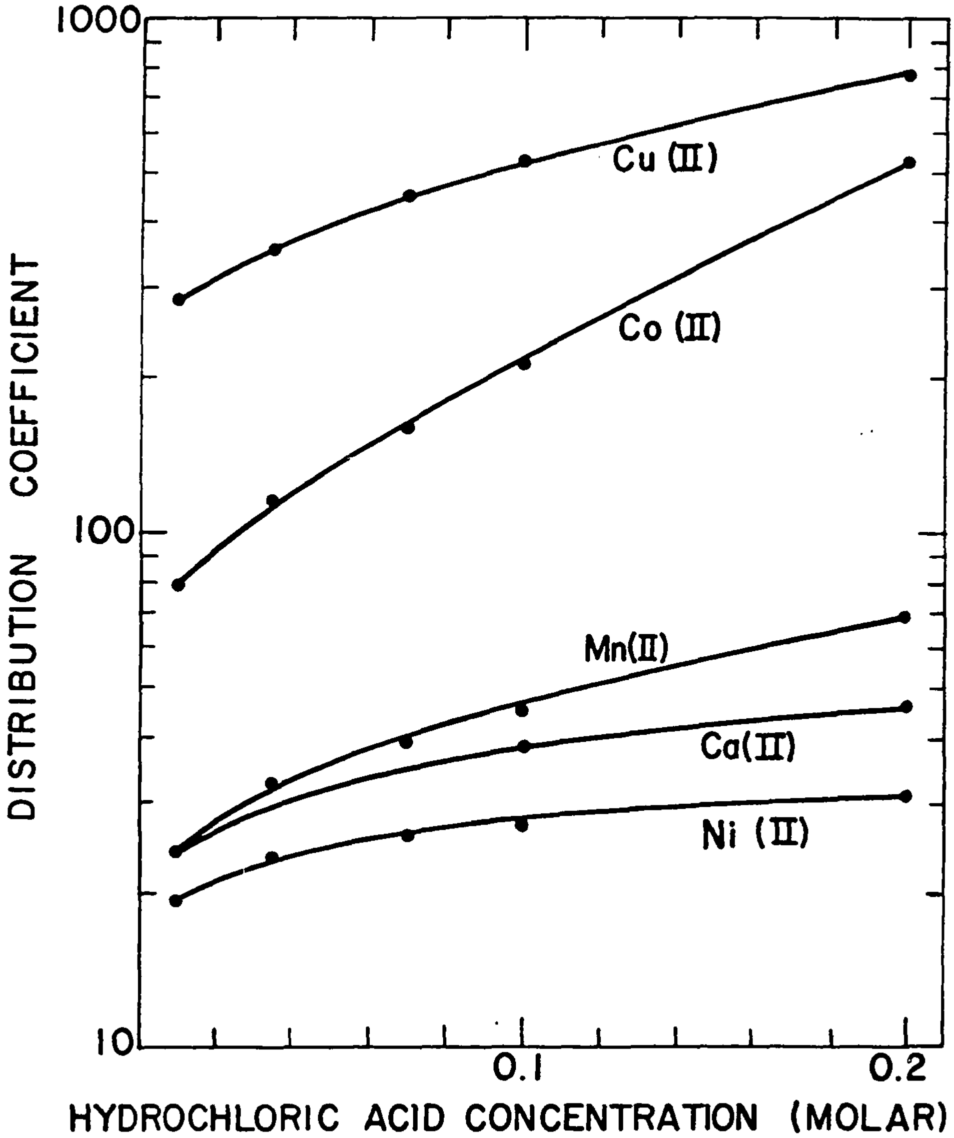

Figure 5. Distribution coefficients of metal chlorides in 90 percent isopropyl alcohol vs. hydrochloric acid concentration

Table 4. Distribution coefficients of metal ions (chloride salts) in 74 percent isopropyl alcohol with varying hydrochloric acid concentration

| (HCl) M | Metal ion | | | | | |
|---|---|---|---|---|---|---|
| | $UO_2$(II) | Co(II) | Th(IV) | Dy(III) | Ni(II) | Ca(II) |
| 0.05 | 6.0 | 0.3 | 0.0 | 0.2 | 0.3 | 0.0 |
| 0.1 | 10.1 | 0.9 | 0.2 | 0.3 | 0.6 | 0.0 |
| 0.5 | 77.0 | 7.2 | 3.9 | 5.0 | 2.8 | 3.1 |
| 1.0 | 441 | 14.8 | 8.5 | 3.9 | 4.7 | 4.8 |
| 1.5 | 1,100 | 48.4 | 10.7 | 6.5 | 5.1 | 6.6 |
| 2.0 | 2,510 | 102 | 12.2 | 8.9 | 6.0 | 7.9 |
| 2.4 | 6.190 | 346 | 18.8 | 10.9 | 6.5 | 8.3 |

Table 5. Distribution coefficients of metal ions (chloride salts) in 65 percent isopropyl alcohol with varying hydrochloric acid concentration

| (HCl) M | Metal ion | | | |
|---|---|---|---|---|
| | Co(II) | Th(IV) | Ca(II) | Ni(II) |
| 0.1 | 0.0 | 0.0 | | |
| 0.5 | 1.1 | 0.0 | | |
| 1.0 | 3.1 | 1.1 | 1.3 | 1.3 |
| 1.5 | 6.1 | 2.1 | 2.1 | 2.4 |
| 2.0 | 15.7 | 3.0 | 2.7 | 2.0 |
| 2.5 | 51.2 | 2.8 | 2.9 | 2.4 |
| 3.0 | 134 | 5.0 | 3.0 | 2.5 |
| 3.5 | 228 | 7.1 | 3.0 | 2.5 |

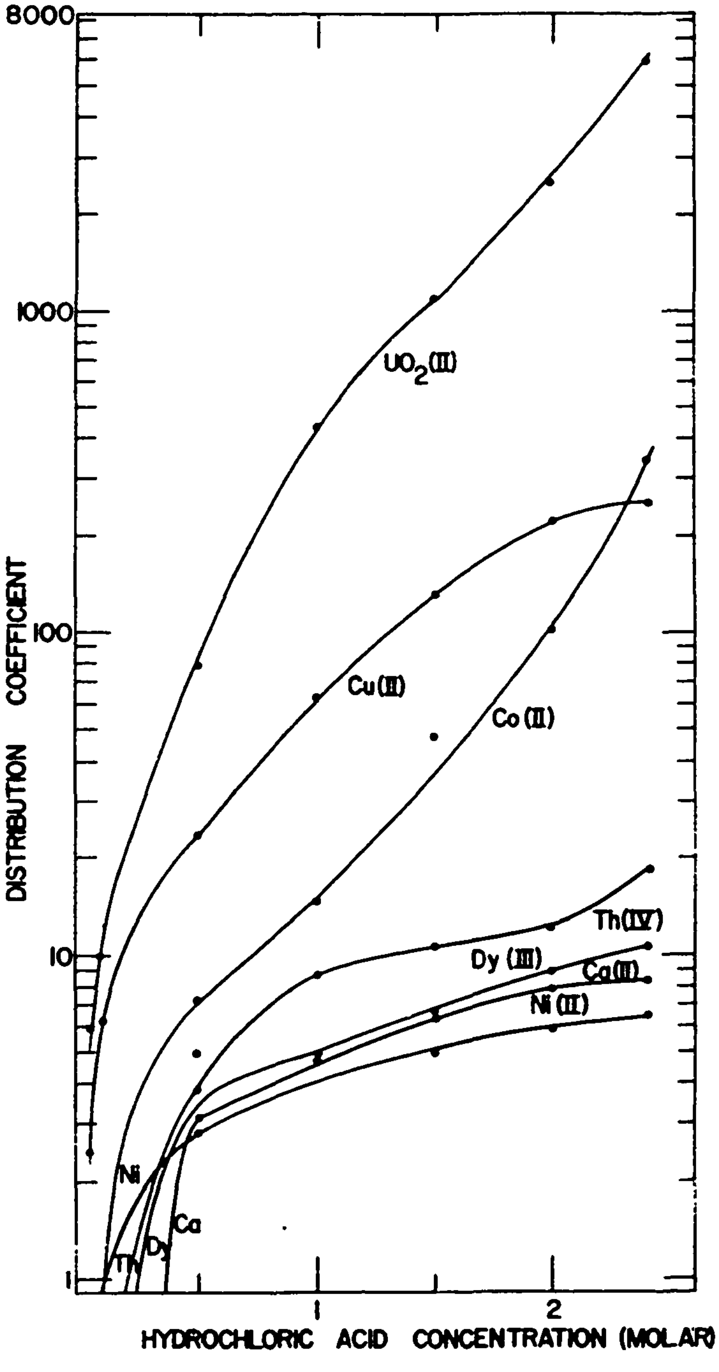

Figure 6. Distribution coefficients of metal chlorides in 74 percent isopropyl alcohol vs. hydrochloric acid concentration

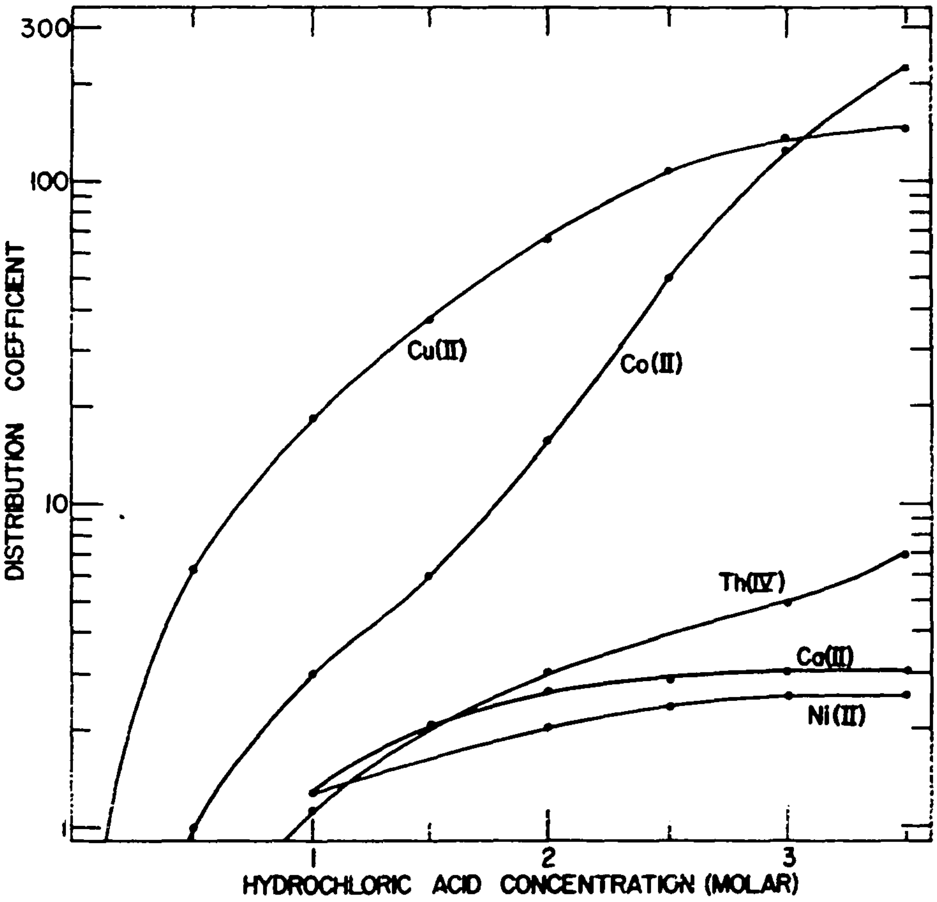

Figure 7. Distribution coefficients of metal chlorides in 65 percent isopropyl alcohol vs. hydrochloric acid concentration

Table 6. Distribution coefficients of metal ions (chloride salts) in 55 percent isopropyl alcohol with varying hydrochloric acid concentration. Strongly adsorbed group

| (HCl) | Metal ion | | | | | | |
|---|---|---|---|---|---|---|---|
| M | Bi(III) | Cd(II) | Zn(II) | $UO_2$(II) | Fe(III) | Co(II) | Mn(II) |
| 0.01 | | 2,070 | 139 | | 0.0 | | |
| 0.05 | 12,200 | 3,590 | 310 | 0.9 | 0.0 | | |
| 0.1 | 9,710 | 5,060 | 467 | 1.4 | 0.0 | | |
| 0.5 | 3,860 | 2,780 | 691 | 7.3 | 4.9 | 0.0 | |
| 1.0 | 4,120 | 1,290 | 606 | 26.4 | 20.7 | 0.6 | 1.1 |
| 1.5 | 1,800 | | | 71.4 | 52.3 | 1.2 | 1.6 |
| 2.0 | 1,360 | 563 | 443 | 204 | 104 | 3.6 | 1.9 |
| 2.5 | | | | 494 | 159 | 9.4 | 2.4 |
| 3.0 | 493 | 335 | 359 | 882 | 187 | 26.4 | 4.3 |
| 3.5 | | | | | | 62.3 | 7.7 |
| 4.0 | 477 | 224 | 268 | 2,310 | 224 | 109 | 14.7 |
| 4.5 | 222 | 197 | | | | 161 | 27.4 |

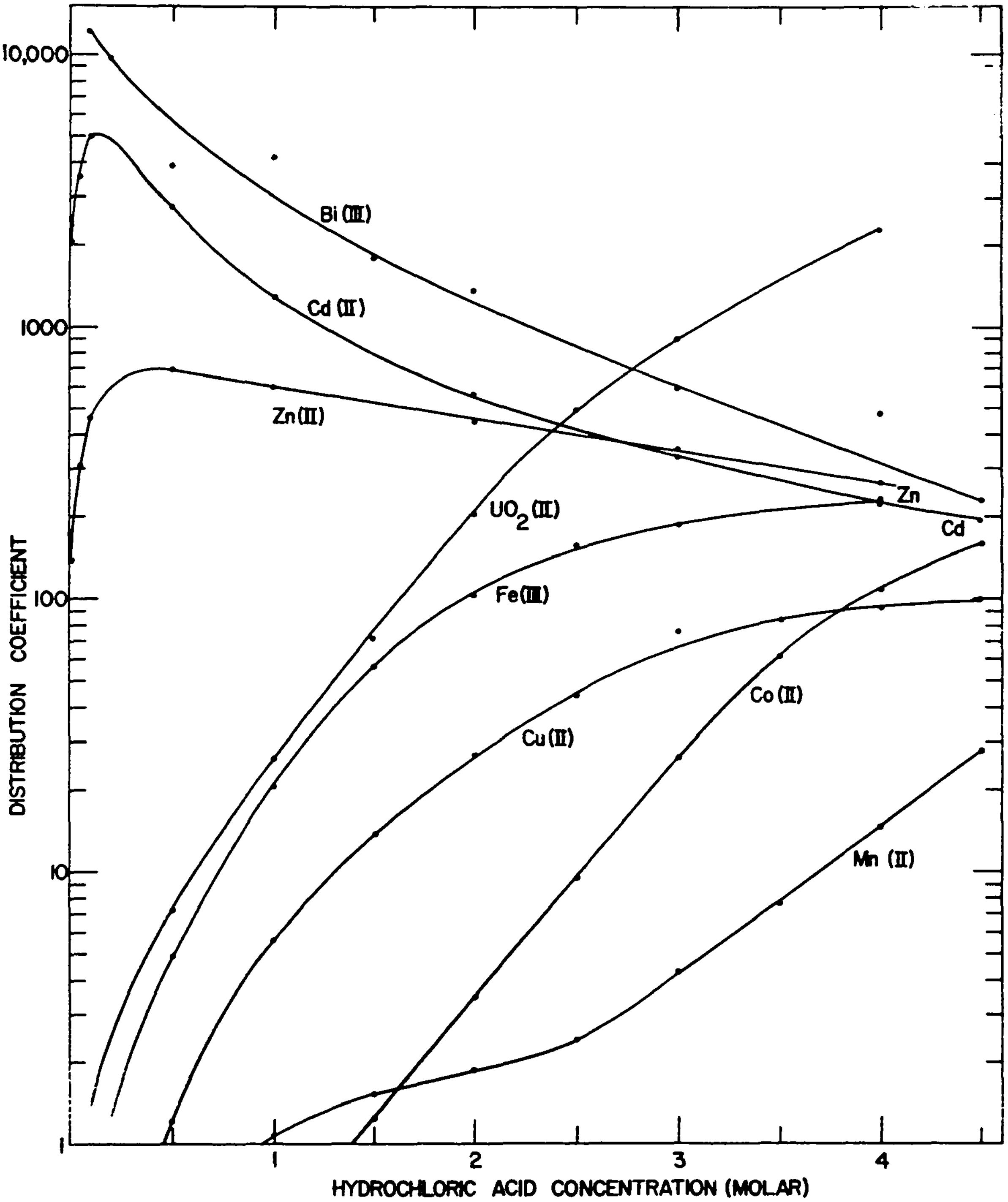

Figure 8. Distribution coefficients of metal chlorides in 55 percent isopropyl alcohol vs. hydrochloric acid concentration. Strongly adsorbed group

Table 7. Distribution coefficients of metal ions (chloride salts) in 55 percent isopropyl alcohol with varying hydrochloric acid concentration. Weakly adsorbed group

| (HCl) | Metal ion | | | | | | |
|---|---|---|---|---|---|---|---|
| M | Cr(III) | VO(II) | Th(IV) | La(III) | ZrO(II) | Ni(II) | Ca(II) |
| 0.5 | 0.8 | 0.4 | 0.0 | 0.0 | 0.0 | | |
| 1.0 | 1.2 | 0.8 | 0.0 | 0.7 | 0.0 | 0.2 | |
| 1.5 | 2.0 | 0.9 | 0.5 | 1.0 | 0.5 | 0.5 | 0.0 |
| 2.0 | 1.8 | 0.8 | 0.6 | 1.3 | 1.3 | | 0.3 |
| 2.5 | 2.0 | 1.3 | 0.3 | | 1.0 | 0.8 | 0.6 |
| 3.0 | 2.0 | 3.4 | 1.1 | 1.6 | 1.6 | 0.8 | 0.6 |
| 3.5 | 1.6 | 3.3 | 1.6 | | a* | 0.8 | 0.2 |
| 4.0 | 3.5 | 3.8 | 1.5 | 1.7 | | 0.9 | 0.3 |
| 4.5 | 6.4 | 4.5 | 2.8 | 1.7 | a* | 0.8 | 0.6 |

*Precipitation occurred

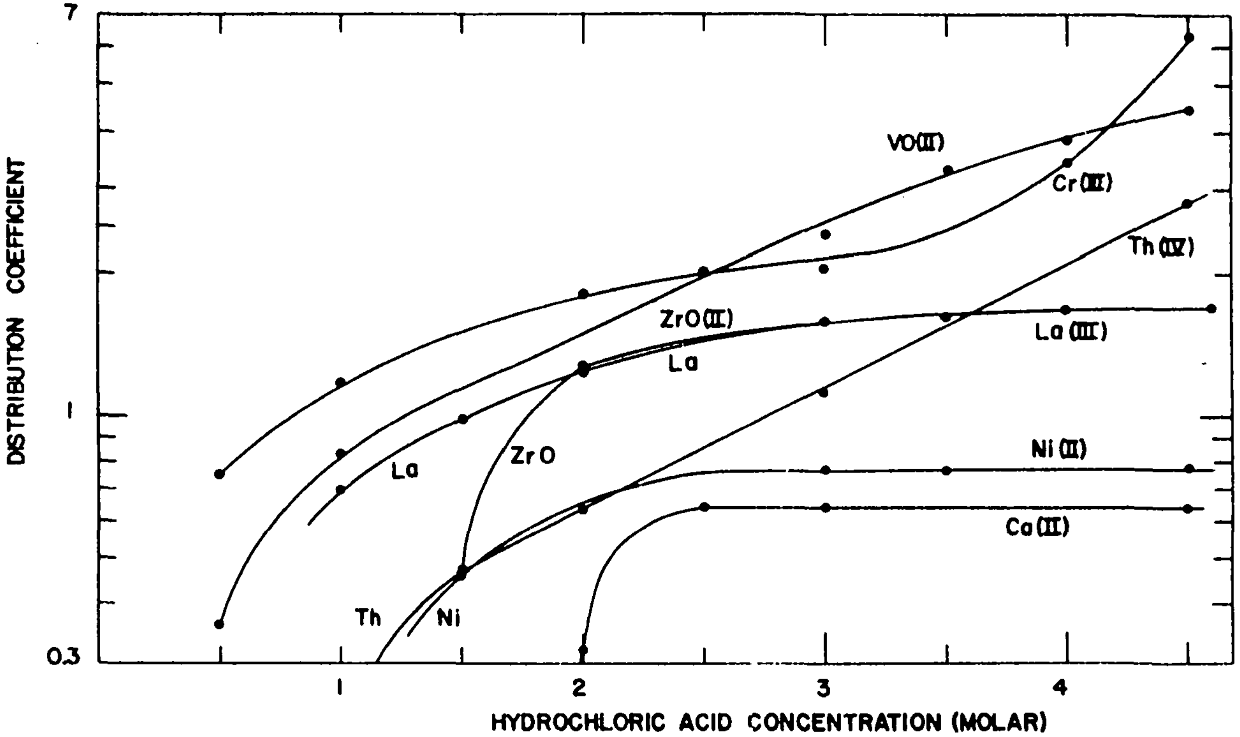

Figure 9. Distribution coefficients of metal chlorides in 55 percent isopropyl alcohol vs. hydrochloric acid concentration. Weakly adsorbed group

Table 8. Distribution coefficients of metal ions (perchlorate salts) in 96 percent isopropyl alcohol with low hydrochloric acid concentration

| (HCl) | Metal ion | | | | |
|---|---|---|---|---|---|
| M | Cu(II) | Co(II) | Mn(II) | Ni(II) | Ca(II) |
| 0.0005 | 2,560 | 1,680 | 85.8 | 12.3 | 13.6 |
| 0.001 | 2,340 | 944 | 26.2 | 13.1 | 13.7 |
| 0.005 | 2,910 | 1,270 | 92.4 | 16.1 | 16.2 |
| 0.01 | 3,670 | 1,420 | 96.0 | 15.4 | 17.4 |

Table 9. Distribution coefficients of metal ions (perchlorate salts) in 97 percent isopropyl alcohol with varying perchloric acid concentration

| $(HClO_4)$ | Metal ion | | | | |
|---|---|---|---|---|---|
| M | Cu(II) | Co(II) | Mn(II) | Ni(II) | Ca(II) |
| 0.02 | 197 | 50.4 | 41.7 | 1.8 | 1.8 |
| 0.035 | 91.8 | 31.7 | 14.6 | 1.4 | 0.1 |
| 0.07 | 43.1 | 22.5 | 7.3 | 0.0 | 0.2 |
| 0.1 | 28.1 | 13.9 | 3.9 | 0.0 | 0.0 |
| 0.2 | 15.3 | 10.4 | 1.3 | 0.0 | 0.0 |

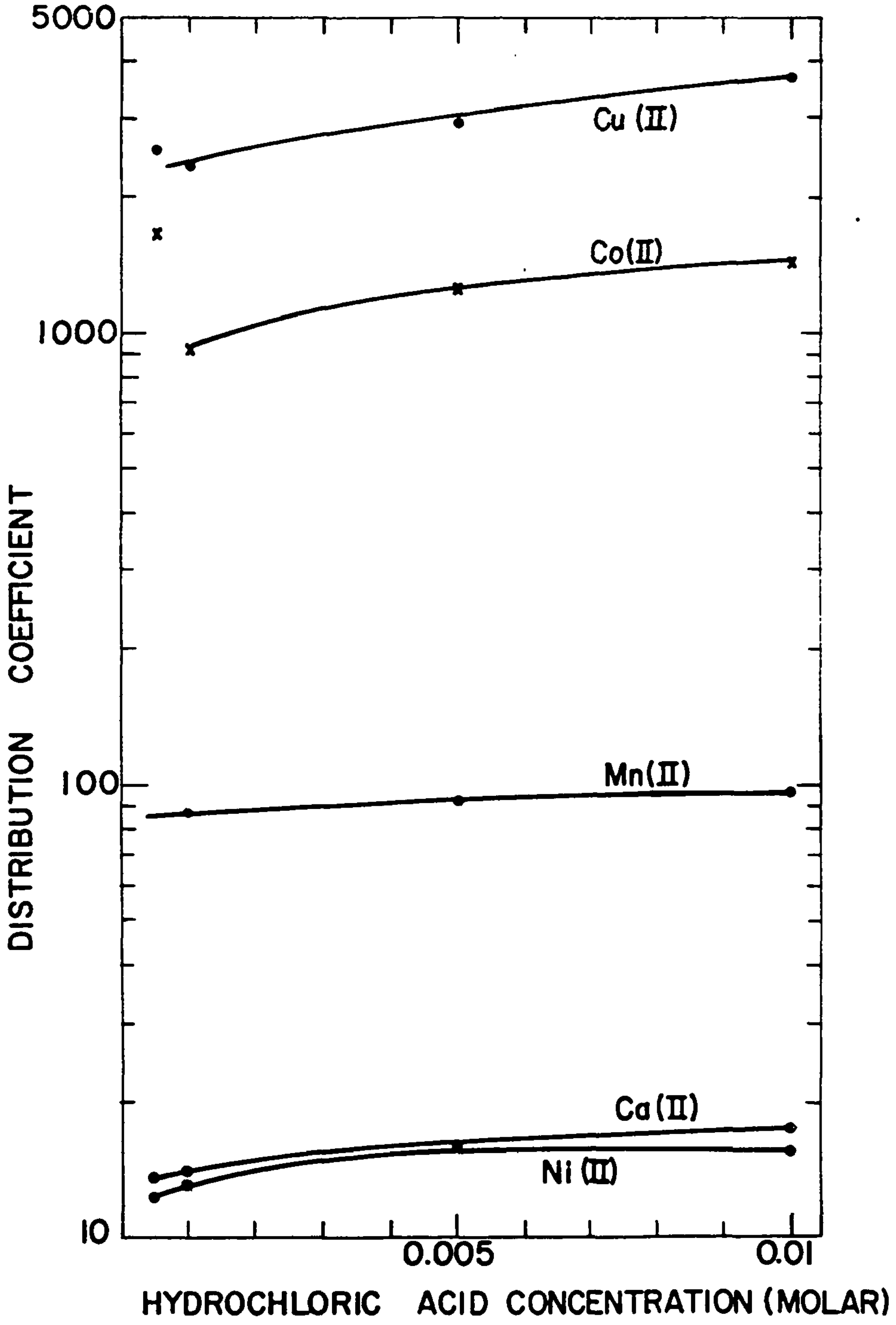

Figure 10. Distribution coefficients of metal perchlorates in 96 percent isopropyl alcohol vs. hydrochloric acid concentration

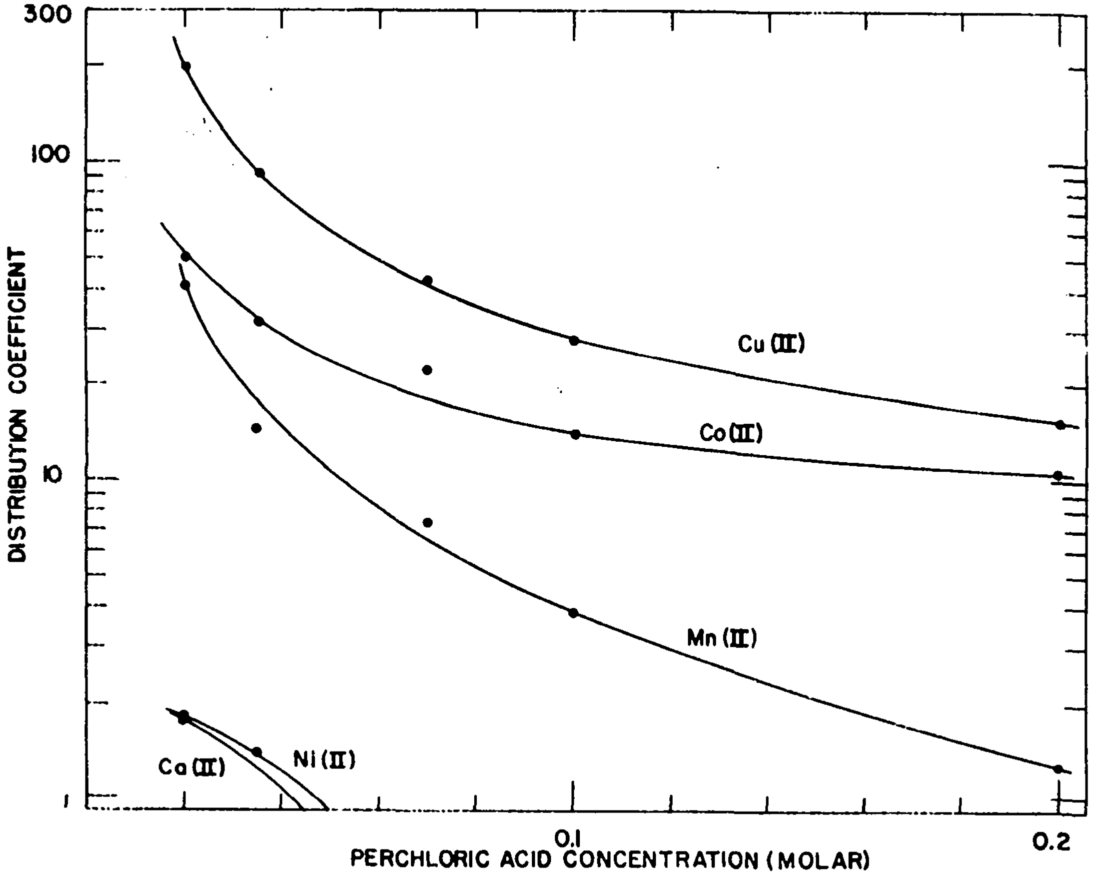

Figure 11. Distribution coefficients of metal perchlorates in 97 percent isopropyl alcohol vs. perchloric acid concentration

Table 10. Distribution coefficients of copper(II) (chloride salt) in 74 percent organic solvent with varying hydrochloric acid concentration

| (HCl) M | Solvent Ethyl alcohol | Acetone | Dioxane | Ethylene glycol |
|---|---|---|---|---|
| 0.05 | 1.2 | 11.9 | | |
| 0.1 | 4.5 | 17.2 | 7.9 | |
| 0.5 | 21.6 | 50.1 | 17.2 | |
| 1.0 | 64.1 | 72.5 | 42.2 | 2.2 |
| 1.5 | 117 | 88.8 | 50.2 | |
| 2.0 | 185 | 117 | 54.7 | 13.8 |

Table 11. Distribution coefficients of copper(II) (chloride salt) in 1.0 molar hydrochloric acid with varying percent of organic solvent

| Solvent % | Solvent Ethyl alcohol | Acetons | Dioxane |
|---|---|---|---|
| 18 | 0.4 | 0.1 | 2.0 |
| 37 | 1.7 | 2.0 | 15.6 |
| 55 | 6.2 | 16.9 | 29.6 |
| 74 | 64.1 | 72.5 | 42.2 |

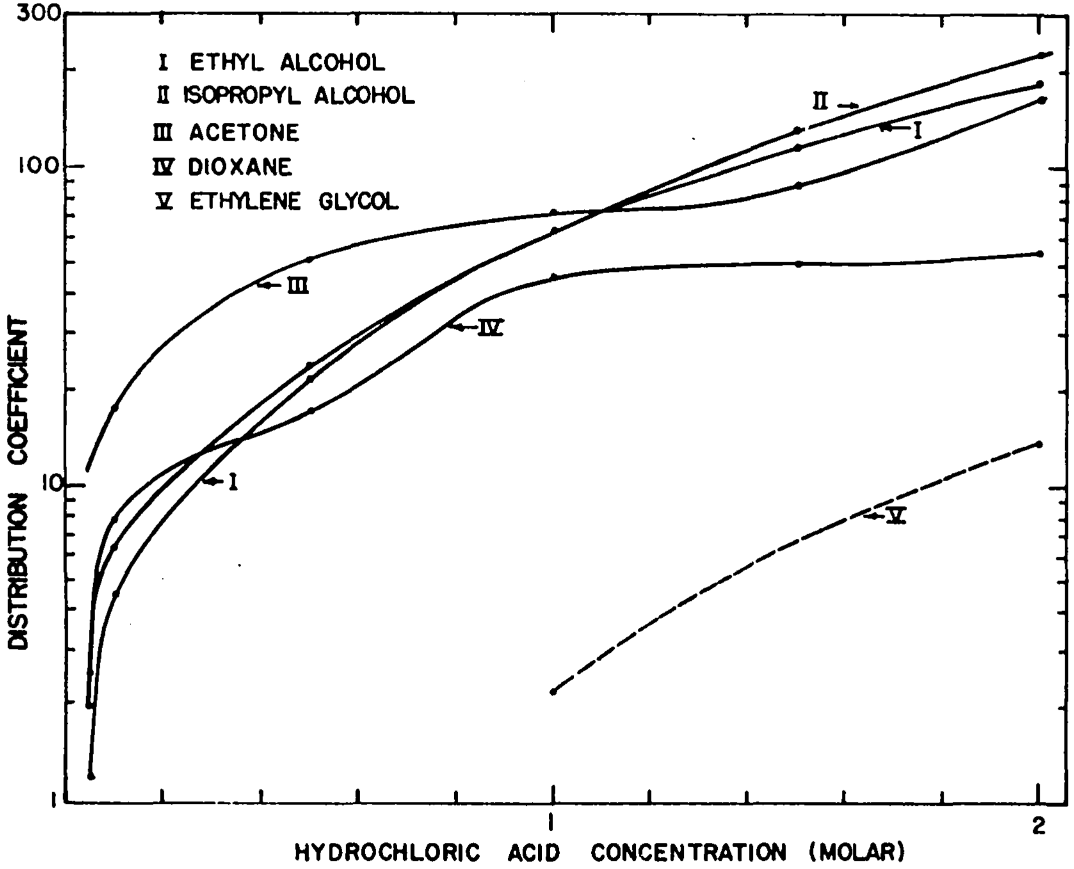

Figure 12a. Distribution coefficients of copper(II) chloride in 74 percent organic solvent vs. hydrochloric acid concentration

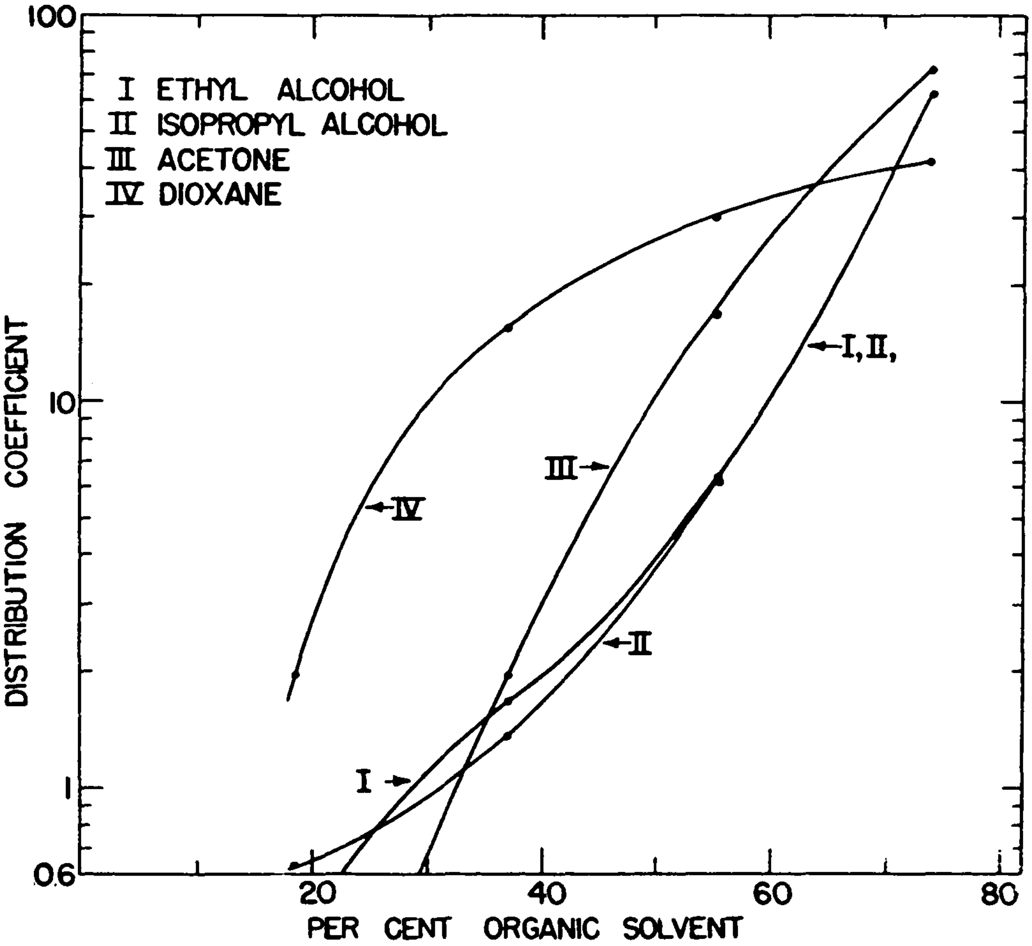

Figure 12b. Distribution coefficients of copper(II) chloride in 1 M hydrochloric acid vs. percent of organic solvent

Table 12. Distribution coefficients of metal ions (perchlorate salts) in 96 percent organic solvent with varying hydrochloric acid concentration

| (HCl) M | Metal ion | | | | |
|---|---|---|---|---|---|
| | Cu(II) | Co(II) | Mn(II) | Ca(II) | Ni(II) |
| | | | Methyl alcohol | | |
| 0.01 | 58.2 | 8.0 | 31.0 | 0.0 | 0.0 |
| 0.05 | 104 | 23.2 | 9.2 | 0.0 | 0.0 |
| 0.1 | 135 | 42.2 | 24.4 | 0.0 | 0.0 |
| 0.2 | 213 | 78.9 | 27.1 | 0.0 | 0.0 |
| | | | Ethyl alcohol | | |
| 0.01 | 1,260 | 246 | 71.0 | 0.2 | 0.7 |
| 0.05 | 1,930 | 772 | 122 | 0.6 | 1.1 |
| 0.1 | 2.530 | 1,790 | 170 | 0.9 | 1.4 |
| 0.2 | 3,440 | 2,260 | 226 | 1.0 | 1.3 |
| | | | Isopropyl alcohol | | |
| 0.01 | 8,970 | 1,420 | 96.0 | 17.4 | 15.4 |
| 0.035 | 8,090 | 1,490 | 118 | 20.0 | 18.0 |
| 0.07 | 8,040 | 6,900 | 127 | 22.4 | 18.4 |
| 0.1 | 8,370 | 6,940 | 114 | 23.7 | 19.2 |
| 0.2 | 8,710 | 2,070 | 117 | 20.3 | 20.5 |
| | | | Acetone | | |
| 0.01 | 7,130 | | | 305 | 522 |
| 0.05 | 3,700 | | | 1,180 | 1,590 |
| 0.1 | 1,480 | | | 843 | 1,080 |
| 0.2 | 720 | | | 338 | 501 |
| | | | Dioxane | | |
| 0.01 | 301 | | 1,240 | 394 | 167 |
| 0.05 | 239 | | 1,160 | 206 | 97.8 |
| 0.1 | 226 | | 1,030 | 102 | 55.6 |
| 0.2 | 203 | | 537 | 158 | 38.6 |

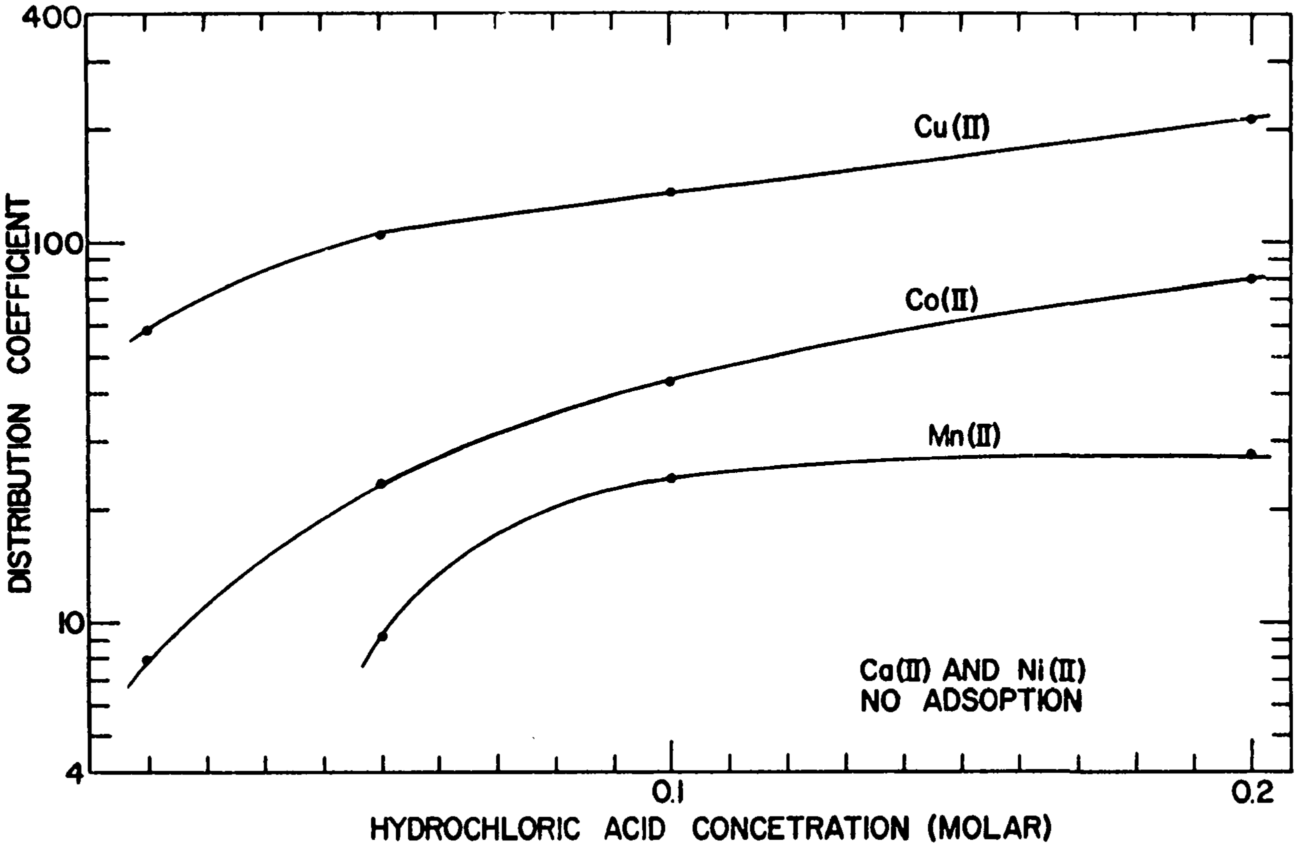

Figure 13. Distribution coefficients of metal perchlorates in 96 percent methyl alcohol vs. hydrochloric acid concentration

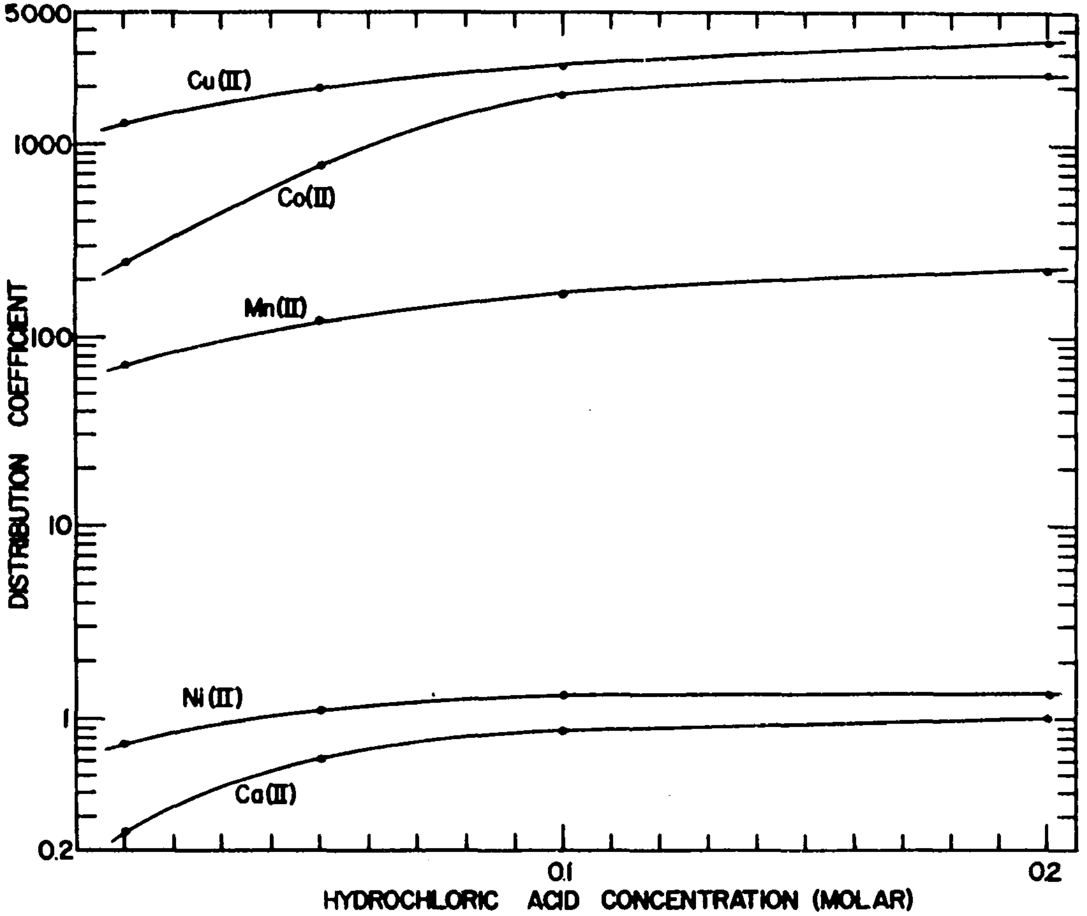

Figure 14. Distribution coefficients of metal perchlorates in 96 percent ethyl alcohol vs. hydrochloric acid concentration

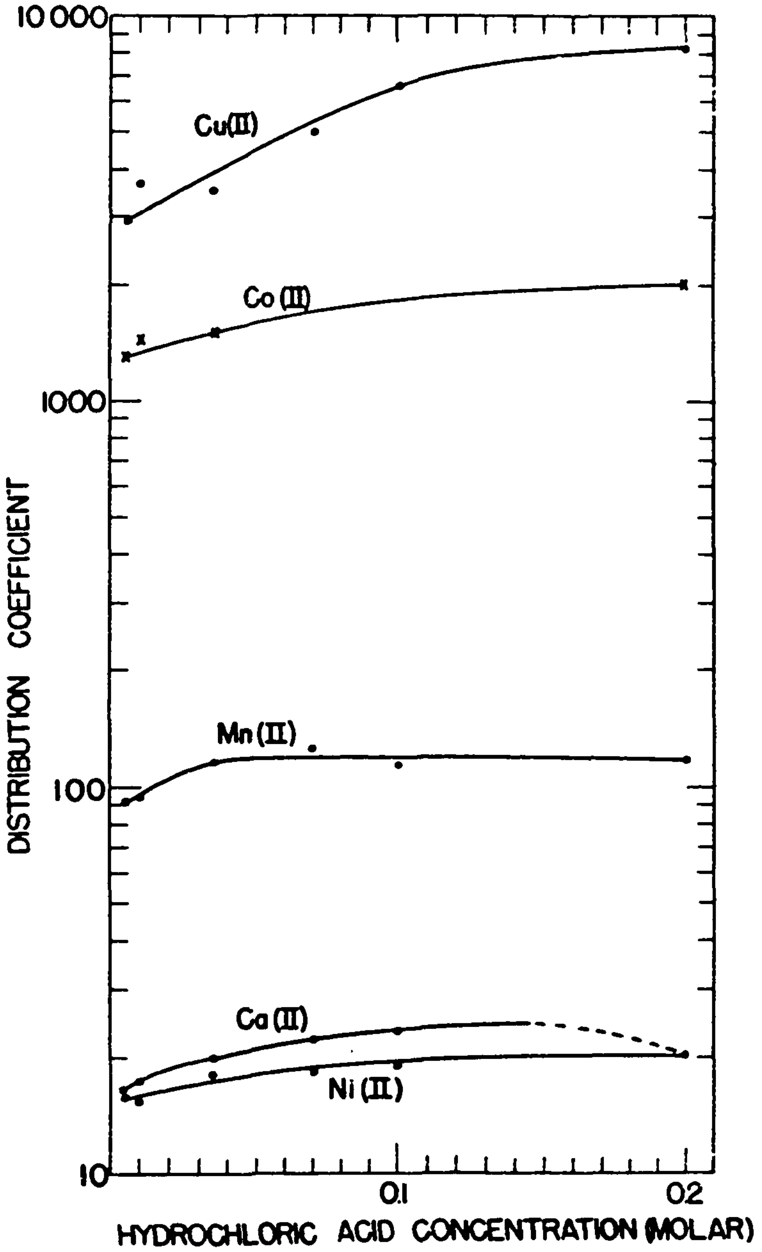

Figure 15. Distribution coefficients of metal perchlorates in 96 percent isopropyl alcohol vs. hydrochloric acid concentration

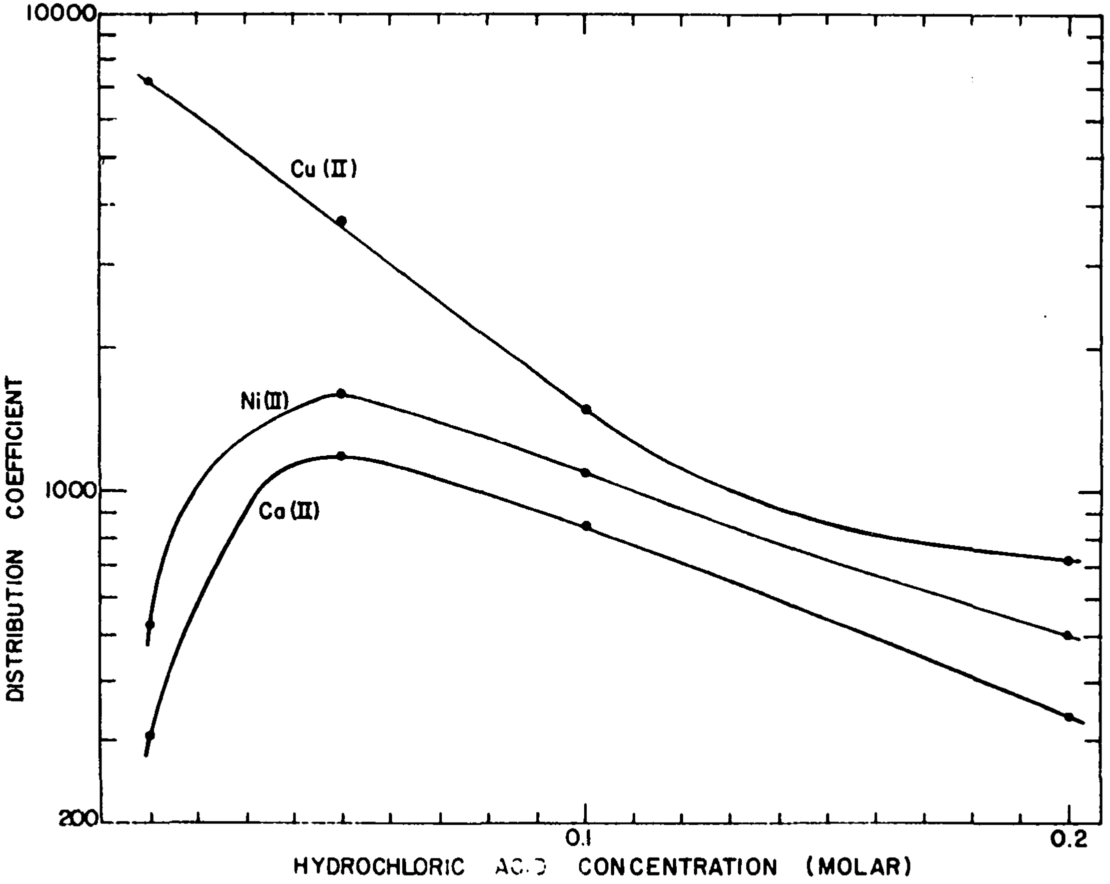

Figure 16. Distribution coefficients of metal perchlorates in 96 percent acetone vs. hydrochloric acid concentration

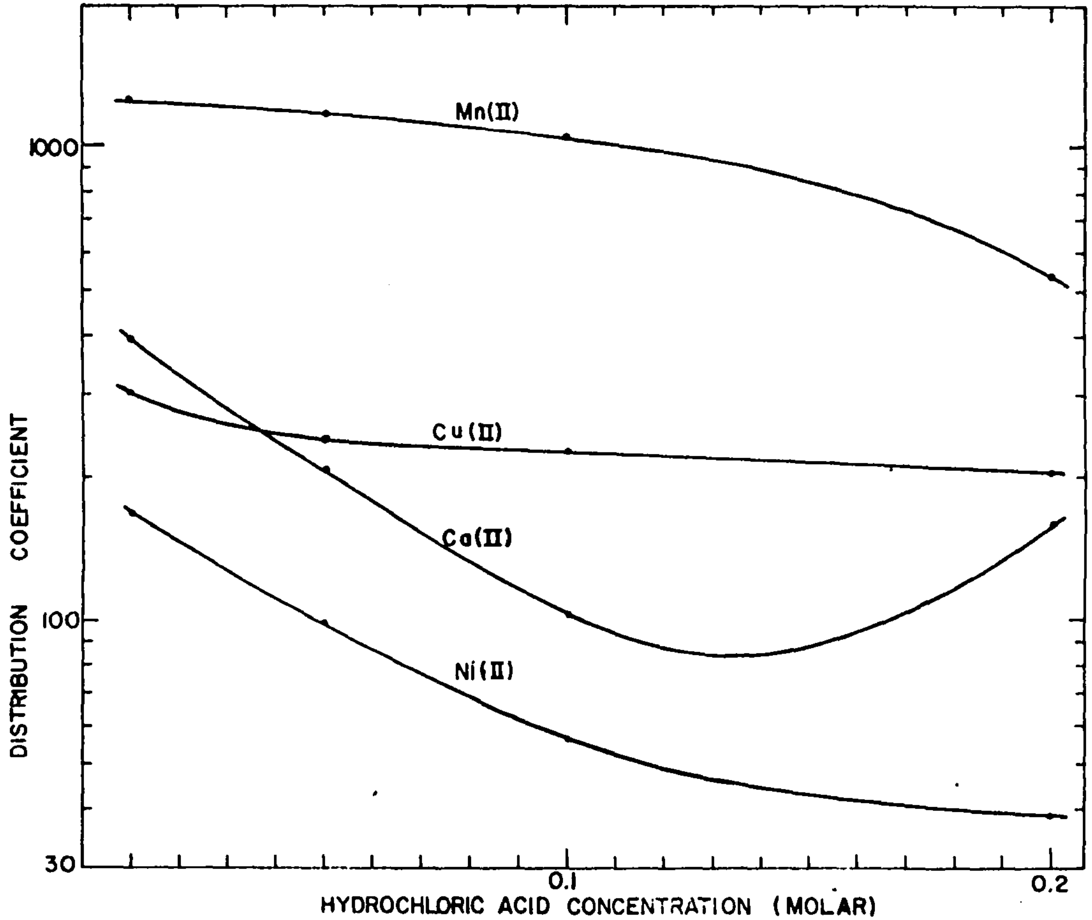

Figure 17. Distribution coefficients of metal perchlorates in 96 percent dioxane vs. hydrochloric acid concentration

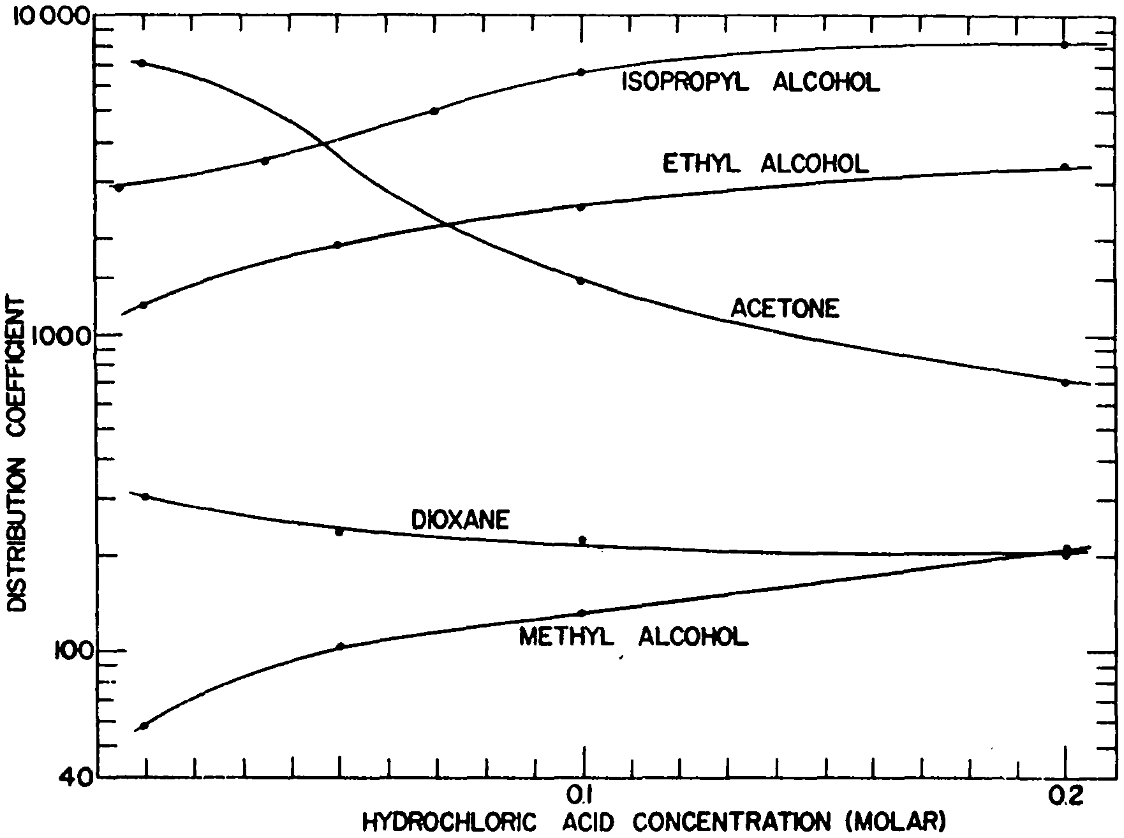

Figure 18. Distribution coefficients of copper(II) perchlorate in 96 percent organic solvent vs. hydrochloric acid concentration

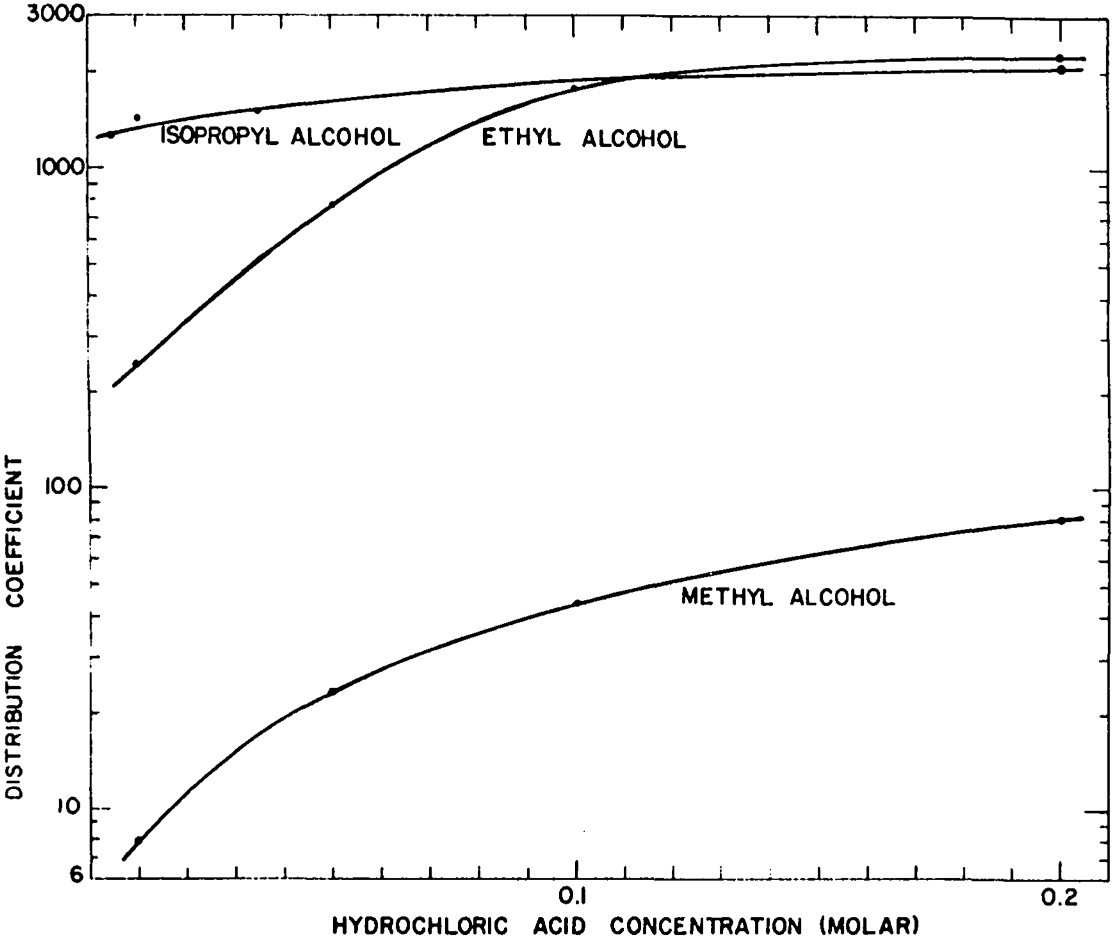

Figure 19. Distribution coefficients of cobalt(II) perchlorate in 96 percent organic solvent vs. hydrochloric acid concentration

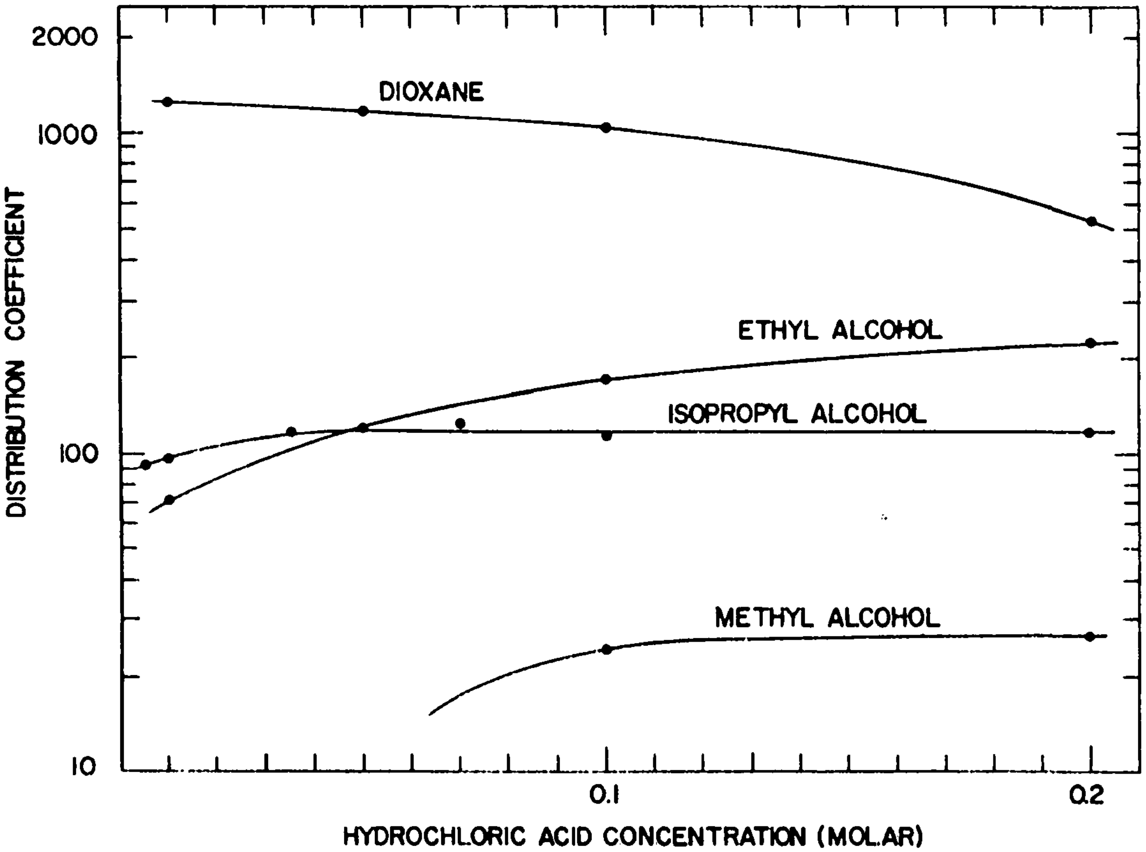

Figure 20. Distribution coefficients of manganese(II) perchlorate in 96 percent organic solvent vs. hydrochloric acid concentration

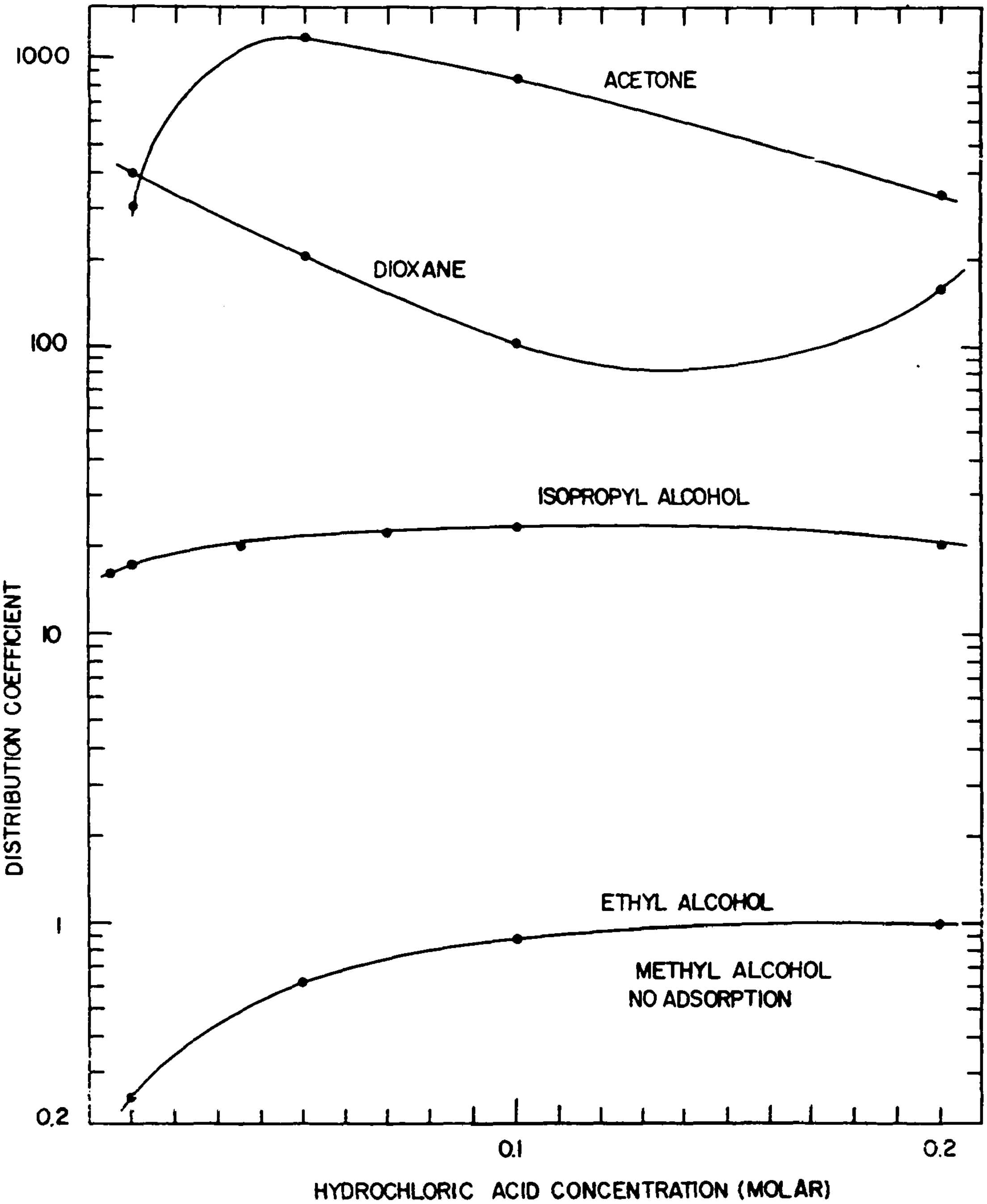

Figure 21. Distribution coefficients of calcium(II) perchlorate in 96 percent organic solvent vs. hydrochloric acid concentration

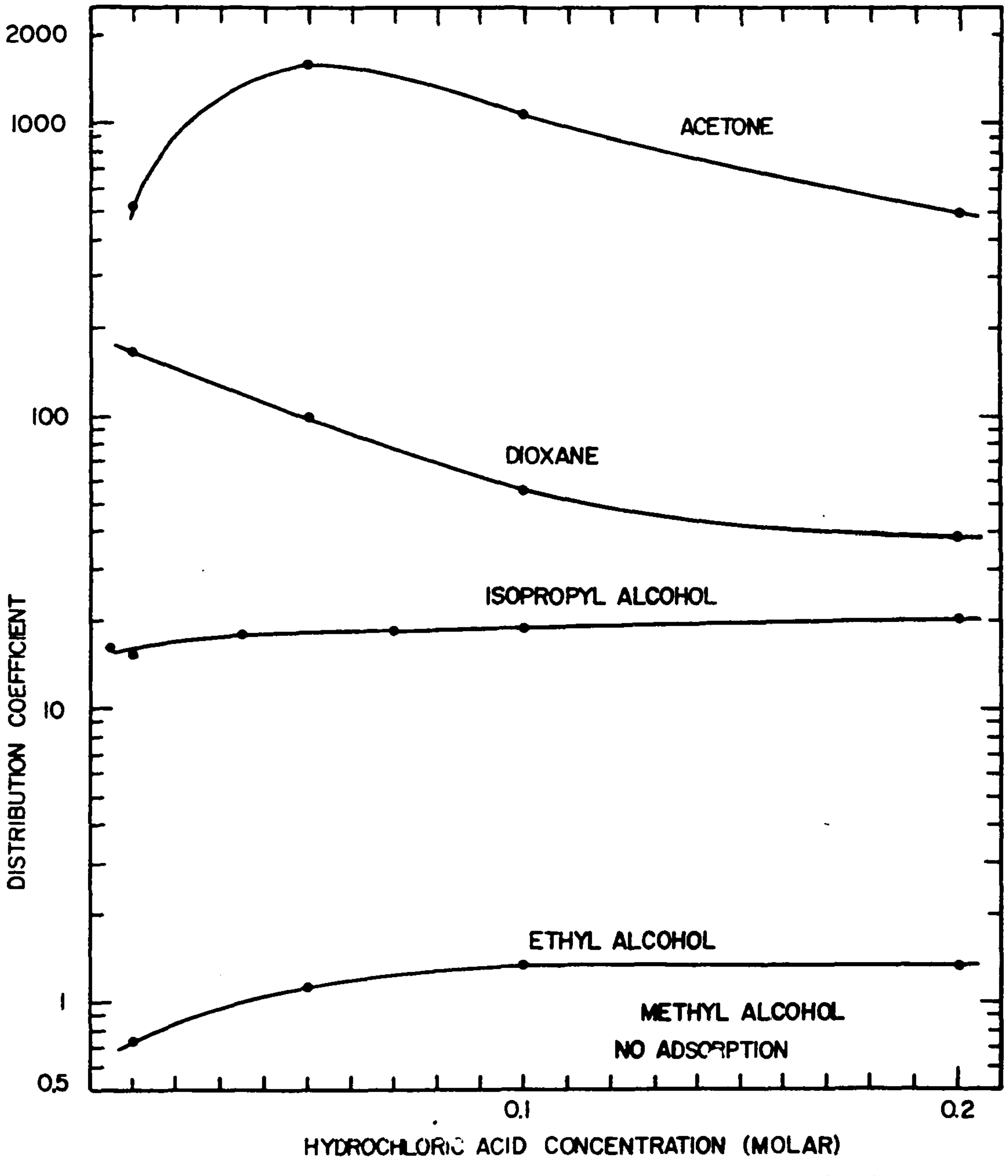

Figure 22. Distribution coefficients of nickel(II) perchlorate in 96 percent organic solvent vs. hydrochloric acid concentration

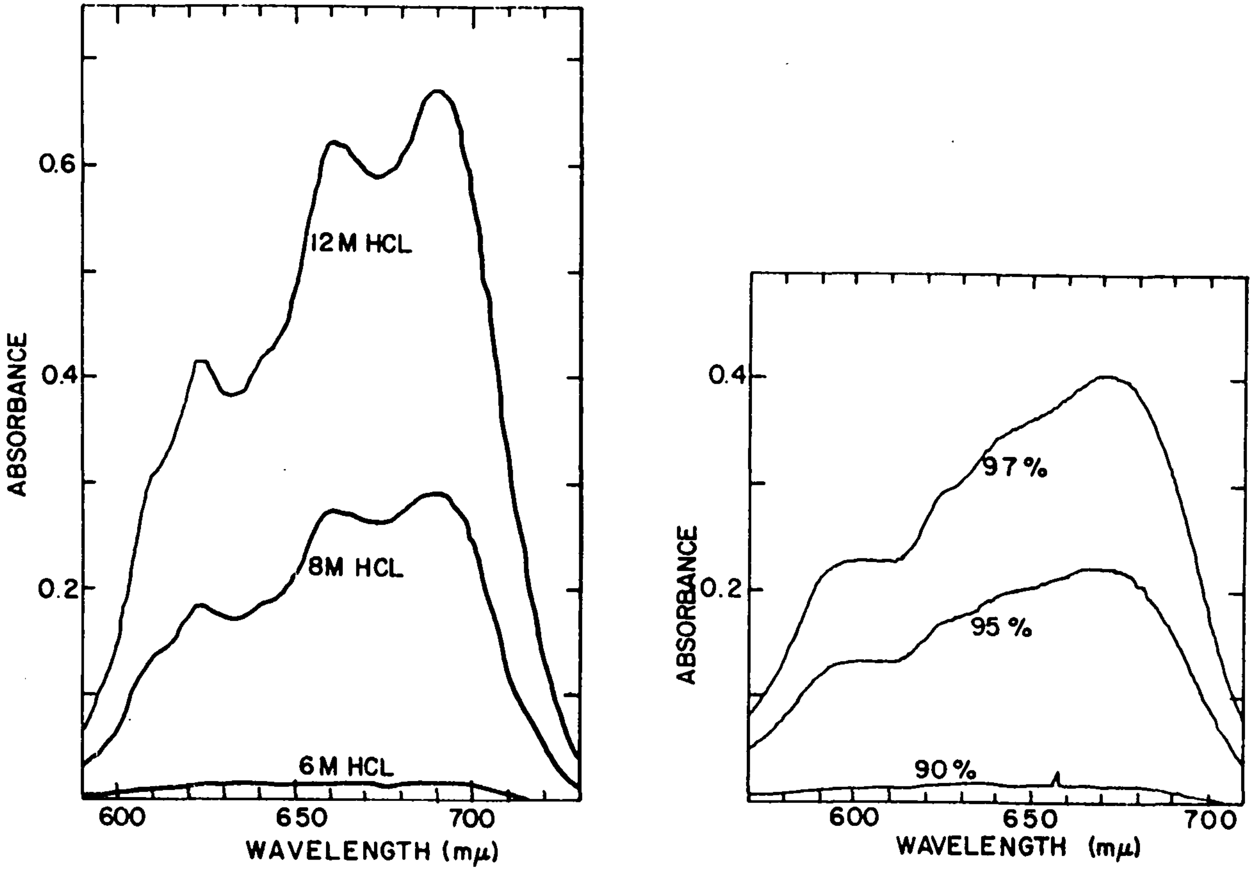

Figure 23. Absorption spectra of cobalt(II) chloride in 0.3 M hydrochloric acid with varying percent of ethyl alcohol (right figure) and in aqueous hydrochloric acid (left figure). One cm. cell and metal ion concentration of 1.16 X $10^{-3}$ M

Table 13. Distribution coefficients of metal ions (chloride salts) in 0.3 molar hydrochloric acid with varying percent of ethyl alcohol. Strongly adsorbed group

| Percent alcohol | Metal ion | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | Bi(III) | Cd(II) | Zn(II) | UO2(II) | Cu(II) | Co(II) | Fe(III) | Mn(II) |
| 30 | | 1,860 | 502 | | | | | |
| 40 | 905 | 3,190 | 589 | | | | 0.0 | |
| 50 | 6,620 | 4,950 | 908 | | 0.4 | | 0.4 | |
| 60 | 4,420 | 5,350 | 636 | 6.1 | 0.3 | 0.0 | 4.2 | 0.0 |
| 70 | 12,000 | 10,700 | 1,720 | 19.1 | 9.9 | 0.1 | 17.4 | 0.7 |
| 76 | | 5,860 | 1,980 | 57.8 | 27.0 | 0.3 | 55.0 | 1.7 |
| 82 | 5,110 | 13,000 | 4,190 | 272 | 96.5 | 16.4 | 142 | 3.7 |
| 86 | | | | 939 | 289 | 75.3 | 286 | 9.7 |
| 90 | 7,650 | 32,300 | 19,300 | 6,670 | 1,290 | 796 | 343 | 50.6 |
| 93 | | 64,500 | | 38,900 | 3,830 | 1,370 | 554 | 405 |
| 95 | 504 | | 67,300 | 85,700 | 7,240 | 6,767 | 699 | 1,950 |
| 97 | | | | | 24,500 | | 969 | 1,950 |

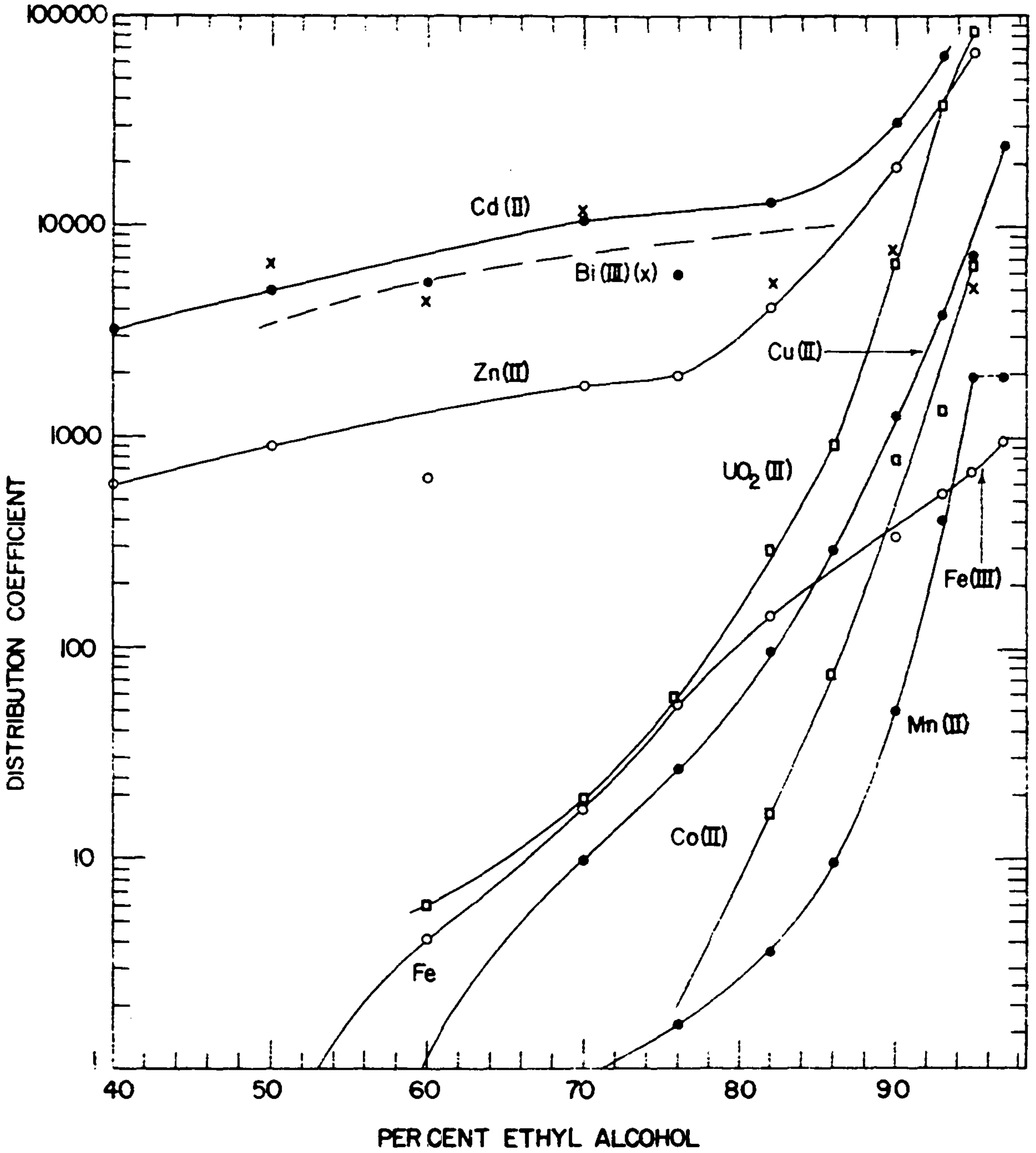

Figure 24. Distribution coefficients of metal chlorides in 0.3 M hydrochloric acid vs. percent of ethyl alcohol. Strongly adsorbed group

Table 14. Distribution coefficients of metal ions (chloride salts) in 0.3 molar hydrochloric acid with varying percent of ethyl alcohol. Weakly adsorbed group

| Percent alcohol | Metal ion | | | | | | |
|---|---|---|---|---|---|---|---|
| | Th(IV) | Dy(III) | La(III) | VO(II) | Cr(III) | Ca(II) | Ni(II) |
| 60 | | 0.0 | 0.0 | | 0.0 | 0.0 | 0.0 |
| 70 | 0.8 | 0.2 | 0.5 | | 0.0 | 0.4 | 0.2 |
| 76 | 1.7 | 1.1 | 1.6 | 0.0 | 0.7 | 1.3 | 0.8 |
| 82 | 2.9 | 3.4 | 3.5 | 0.1 | 0.9 | 2.6 | 1.6 |
| 86 | 8.9 | 6.0 | 7.4 | | 0.0 | 4.0 | 2.5 |
| 90 | 17.6 | 13.0 | 15.5 | 0.0 | 3.7 | 5.6 | 3.2 |
| 93 | 65.7 | 16.1 | 22.1 | 2.8 | 6.8 | 5.4 | 3.1 |
| 95 | 38.1 | 16.5 | 21.4 | 3.6 | 2.6 | 4.1 | 3.8 |
| 97 | 92.6 | 22.9 | 19.8 | 5.6 | 1.1 | 1.5 | 3.3 |

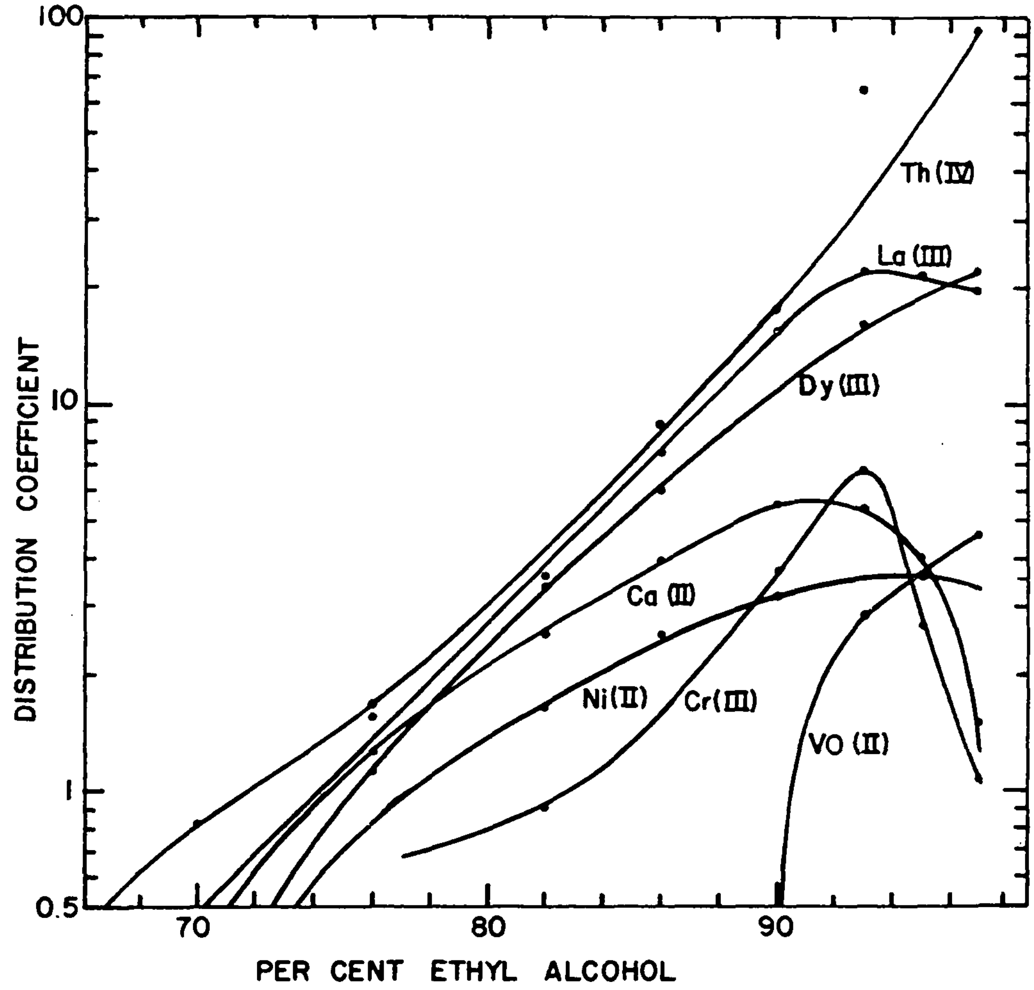

Figure 25. Distribution coefficients of metal chlorides in 0.3 M hydrochloric acid vs. percent of ethyl alcohol. Weakly adsorbed group

Table 15. Distribution coefficients of metal ions (chloride salts) in 0.2 molar hydrochloric acid with varying amounts of methyl and ethyl alcohol totaling 96 percent

| Percent methyl alcohol | Percent ethyl alcohol | Metal ion | | | | |
|---|---|---|---|---|---|---|
| | | Ni(II) | Ca(II) | Dy(III) | Th(IV) | Sc(III) |
| 0 | 96 | 3.4 | 2.8 | 21.0 | 92.5 | |
| 10 | 86 | 1.3 | 1.2 | 13.6 | 58.7 | 11.1 |
| 29 | 67 | 0.2 | 0.1 | 4.0 | 29.9 | 5.4 |
| 48 | 48 | 0.0 | 0.0 | 1.1 | 12.8 | 2.5 |
| 67 | 29 | 0.0 | 0.0 | 0.3 | 6.1 | 1.5 |
| 86 | 10 | 0.0 | 0.0 | 0.0 | 2.9 | 0.5 |
| 96 | 0 | 0.0 | 0.0 | 0.0 | 2.1 | 0.5 |

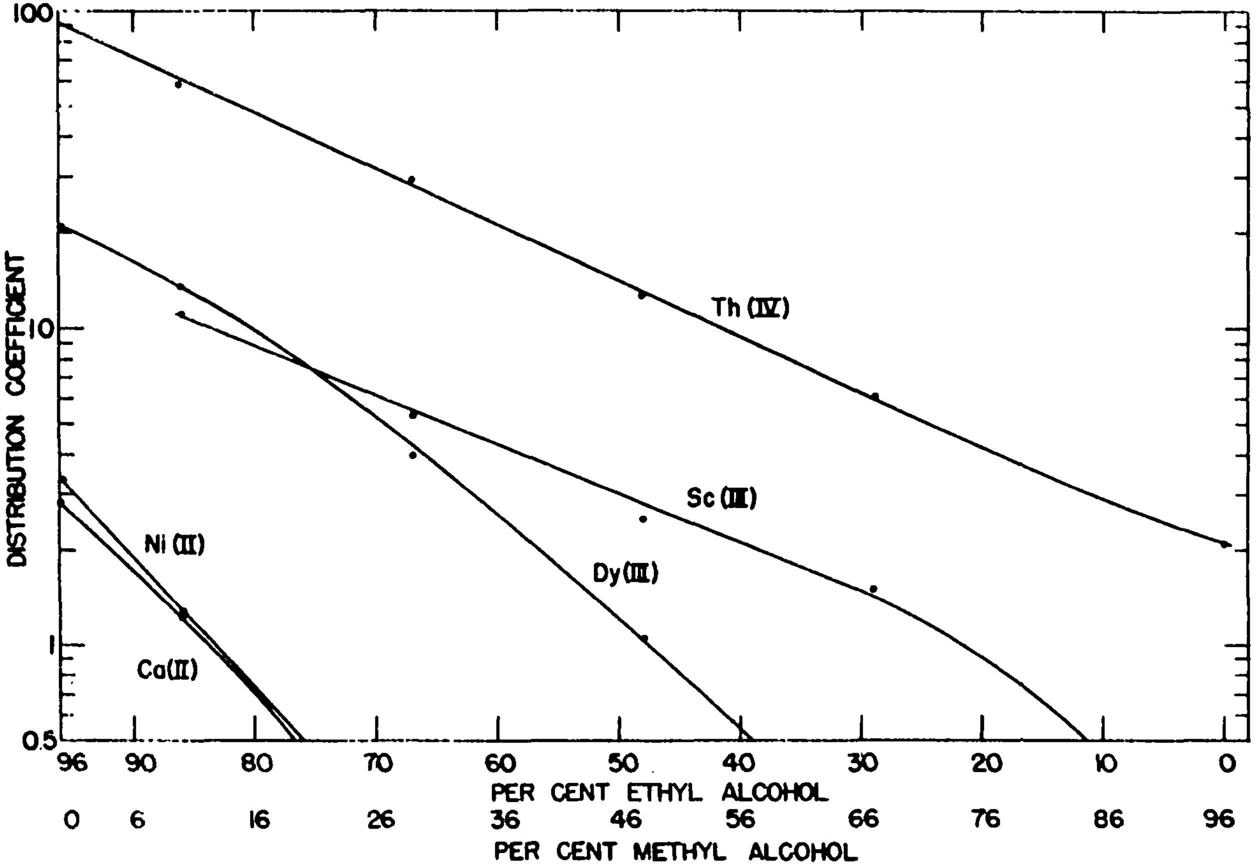

Figure 26. Distribution coefficients of metal chlorides in 0.2 M hydrochloric acid vs. mixed methyl and ethyl alcohol totaling 96 percent

Table 16. Distribution coefficients of metal ions (chloride salts) in 0.2 molar hydrochloric acid with varying amounts of methyl and isopropyl alcohol totaling 96 percent

| Percent methyl alcohol | Percent isopropyl alcohol | Metal ion | | | | |
|---|---|---|---|---|---|---|
| | | Ni(II) | Ca(II) | Dy(III) | Th(IV) | Sc(III) |
| 0 | 96 | 64.0 | 110 | | | |
| 14 | 82 | 22.0 | 29.8 | 20.3 | 148 | 48.5 |
| 34 | 62 | 3.2 | | 18.1 | 73.4 | 21.0 |
| 48 | 48 | 0.8 | 1.0 | 8.2 | 50.6 | 10.1 |
| 62 | 34 | 0.4 | 0.2 | 0.3 | 17.3 | 4.6 |
| 77 | 19 | 0.3 | 0.0 | 0.2 | 9.4 | 1.8 |
| 86 | 10 | 0.2 | | 0.1 | 3.5 | 1.0 |
| 91 | 5 | 0.1 | 0.0 | 0.0 | 2.6 | 0.9 |
| 96 | 0 | 0.0 | 0.0 | 0.0 | 2.1 | 0.5 |

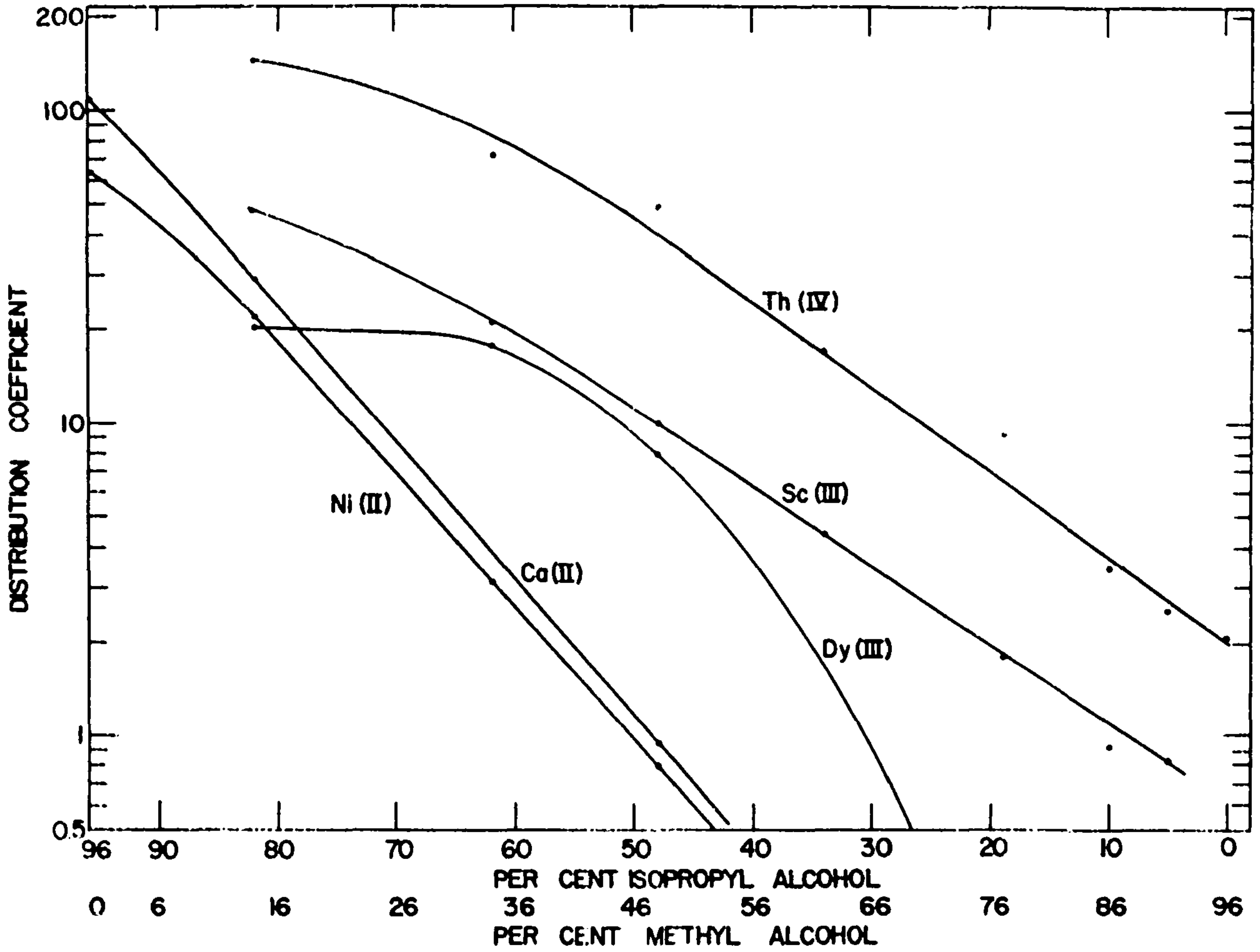

Figure 27. Distribution coefficients of metal chlorides in 0.2 M hydrochloric acid vs. mixed methyl and isopropyl alcohol totaling 96 percent

## SEPARATIONS

The selection of column operating conditions is often a matter of guesswork and usually results in over separation, thus taking up more time than is necessary. Cornish (74) developed a practical application of chromatographic theory to analytical separations in ion exchange. In the elution method the species to be separated are adsorbed from a small volume to form a narrow band at the top of a column. Upon elution the bands will move down the column separating in accordance with their respective distribution coefficients. A typical result which shows the concentration of each species leaving the column is illustrated in Figure 28. In this Figure the symbols are defined as follows:

$D$ = Distribution coefficient

$V$ = Residual volume of liquid in column before elution

$V_1$ = Volume required to elute to peak 1

$V_2$ = Volume required to elute to peak 2

$m_1$ = Equivalents of solute 1

$m_2$ = Equivalents of solute 2

$\Delta m_1$ = Equivalents of $m_1$ in solute 2 fraction

$\Delta m_2$ = Equivalents of $m_2$ in solute fraction

$a = D + 1$

$W$ = Width of the peak at 0.368 of the peak height

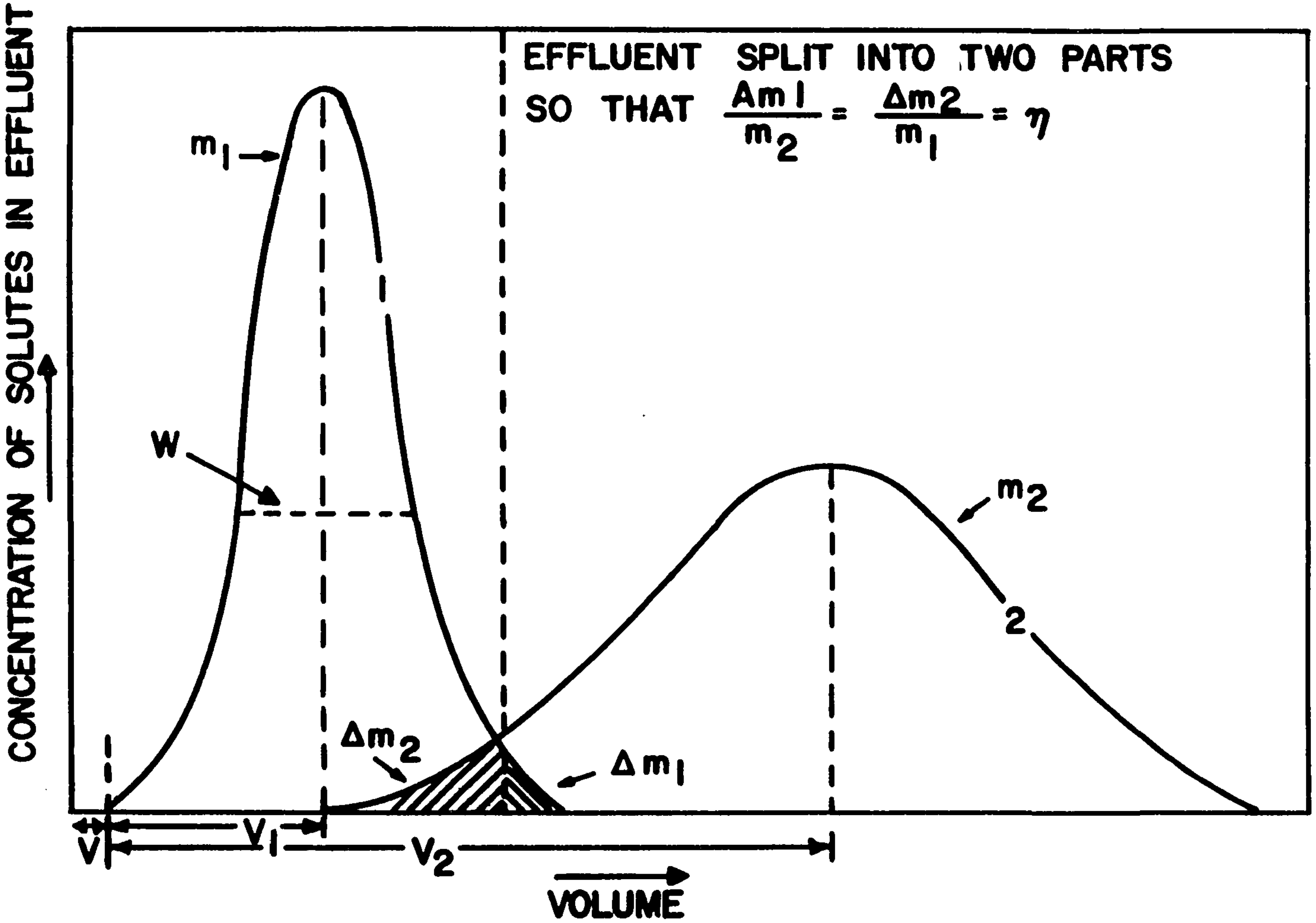

Figure 28. Typical elution curves for the separation of solute 1 and solute 2

The cross-contamination between the two peaks depends on (1) the volume between the peak maxima, and (2) the shape and width of each peak. These two factors are almost completely independent and thus can be considered separately.

The volume required to elute a solute is governed by the rate at which the solute band moves down the column, and this in turn depends on the distribution of the solute between the resin and the eluting solution. This distribution is determined, among other factors, by the equilibrium distribution coefficient (see previous section for discussion of distribution coefficient). An increase in the ratio of $V_2$ to $V_1$ or of the ratio of the distribution coefficients gives rise to greater separation of the species. This ratio or separation factor, $\alpha$, is the most important factor in elution chromatography.

Symmetrical peaks are desirable because any extensive trailing edges increases the cross-contamination between neighboring peaks. To achieve this Gaussian elution curve, column loading must be in the order of 50 mg. per sq. cm. or less. The width of the eluted peak is related to the number of theoretical plates, N, by the following equation

$$N = \frac{8(V + V_n)^2}{W^2} = \frac{L}{h} \qquad (18)$$

where W is the width of the peak at 0.368 of the peak height, L is the length of the resin bed, h is the height equivalent to a theoretical plate and V and $V_n$ (nth peak) are the volumes as designated previously. The height equivalent to a theoretical plate is that length of column from which the solution leaving the exit end is in equilibrium with the resin at the entrance end. The smaller the height the better the separation as each peak becomes narrower and less overlap occurs.

In practice, the separation factor is usually known rather than the elution curves. A problem arises in selection of the proper column parameters such as resin size, flow rate, and length of column. Cornish used previously published data to correlate all of these parameters in such a manner that by a few simple calculations and graphical interpretation this problem is greatly simplified. The cross-contamination, $\eta$, is given by the ratio of $\Delta m_2$ to $m_1$ (see Figure 28 and terminology). $\eta$ is calculated on the assumption that the effluent from the column is divided into two portions to give products of equal purity, i.e. $\frac{\Delta m_2}{m_1} = \frac{\Delta m_1}{m_2}$. The percent of purity of each solute is then $100(1 - \eta)$. The ratio of $(D_2 + 1)$ to $(D_1 + 1)$ (or $a_2/ a_1$) is related to the number of theoretical plates, graphically, by the parameter $\frac{\eta(m_1^2 + m_2^2)}{2m_1m_2}$. Similarly, an empirical relationship between the height equivalent to a theoretical plate and particle size of the resin was done graphically by a family of curves. These curves are defined by different flow rates of the eluting agent.

All of the calculations are extremely simple. The column diameter is determined by the total mass to be separated and the 50 mg. per sq. cm. loading rule. The flow rate and resin particle size are selected, and from this the height equivalent to a theoretical plate is determined. From the required purity desired and calculations of the $a_2/a_1$ ratio and $\eta$ parameter, the number of plates, N, is determined. Multiplication of these two terms then yields the length of resin necessary for the separation.

In applying these selected conditions three rules must be kept in mind. (1) The height equivalent to a theoretical plate obtained from the curves may differ from practical results by a factor of up to 3. This is caused by unknown variables such as non-uniform shape of the resin particles ununiform crosslinking or inefficient column packing. (2) The curves serve essentially as a guide; the actual column must be slightly over designed to ensure adequate separation. (3) The curves may be considerably in error when applied to anion resins if used in strong acid.

Of particular importance to this work are rules (1) and (3). Fortunately, Cornish compared the height equivalent to a theoretical plate found by experiment to that found by calculation for a number of separations using anion exchange resins ( also for cation resins). From this, an empirical factor can be introduced to correct, roughly, the calculated height.

This method served as a useful guide for the selection of flow rate and column dimensions in the separations to be described. Rigid application was not followed, principally because most of the separations have very favorable separation factors. Therefore, in most cases, the column of resin was moderately overdesigned. In addition to the calculations, other factors, which are discussed in the following paragraphs, were also considered in the selection of the column parameters.

The extent of cross-linkage was considered in selecting the proper resin. This is very important as it controls the swelling properties of the resin. In general, as the cross-linking increases the swelling decreases. It must also be remembered, however, that the exchange equilibrium decreases with increased cross-linkage. Thus selection of a resin with optimium cross-linking is important. It was expected that some contraction or expansion of the resin columns would occur as the eluting agents were changed. This is because these changes usually involve a significant change in the water content as well as the hydrochloric acid content. In practice, expansion is encountered much more than contraction. This expansion is undoubtedly due to the resin absorbing the more polar species, water and hydrochloric acid, because the eluting sequence is towards a water-hydrochloric acid eluting system. With these facts in mind the 8 percent cross-linked resin was selected.

The distribution coefficients were determined using Dowex 1 X8, chloride form, 100 to 200 mesh resin. This resin was also used in the preliminary separation studies. It was found that the bands of metal ions on the column were spread out. This spreading, however, was not large enough to prevent the use of the 100 to 200 mesh resin for separations. But, it would require longer columns of resin and consequently, larger volumes of eluting agent. Shortening of the bands can be accomplished by using a finer mesh resin as these will reach equilibrium more rapidly. For this reason the 200 to 400 mesh resin was selected for the separations.

Separations are achieved by adsorption of the elements on the resin at low hydrochloric acid concentration and high ethyl alcohol concentration, followed by elution with solutions of progressively lower hydrochloric acid concentration in constant water-organic solvent compostions or by progressively lower ethyl alcohol concentrations with constant hydrochloric acid concentration. Exchange was carried out under conditions whereby the distribution coefficients are maximal and conditions for removal were selected so that the distribution coefficient of one element at a time became one or close to one, while those for the other elements remained as high as possible. Using these principles, innumerable separations may be devised from Figure 8 and 9, 24 and 25, and 26. Small columns and small volumes of eluent will usually be sufficient for the separations.

Initial separations were by the elution scheme suggested in Figure 24 and 25 (constant hydrochloric acid concentration with varying percent of ethyl alcohol). Column parameters were calculated according to the previously described method of Cornish. The examples in Table 17 illustrate the elution order, quantity of eluent needed, and separation and recovery for synthetic methal ion mixtures. The sample was introduced by the pipetting technique. In all cases Dowex 1 X8, 200 to 400 mesh, chloride form resin was used with a flow rate of approximately 0.25 ml. per minute. The column dimensions and sample sizes are given in parentheses in the Table. Elution of the metal ion mixtures, which are approximately 1:1 ratios by weight, are given in their respective elution order. Also included is the volume of wash solution that was collected with the first eluted metal ion.

Several separations are not possible using this elution scheme. Uranium(VI), copper(II), and iron(III) can be separated only as a group. Nickel(II), calcium(II), vanadium(IV), and chromium(III) can also only be separated as a group. Manganese(II) can be separated from this latter group but the separation is only moderately successful. The separation is done with a 95 percent ethyl alcohol-0.3 M hydrochloric acid eluting agent. It is seen in the distribution coefficient curves (Figure 24 and 25) that this latter [nickel(II) etc.] group has distribution values of about 4 to 5 in this eluting medium. Considerable tailing occurs which then necessitates excessive amounts of eluting agent (see Ni(II)-Mn(II) separation in Table 17). Also, manganese(II) cannot be separated from cobalt(II). Another group separation is bismuth (III), cadmium(II), and zinc(II).

The technique of chromatographic separation is possible because in some cases there is significant difference in the distribution coefficients. This would require considerably longer columns and greater amounts of eluting agents. A good example of this is the possible separation of a mixture containing thorium(IV), rare earths(III), and the nickel group. The distribution coefficients in 95 percent ethyl alcohol -0.3 M hydrochloric acid, which would be the eluting agent, are 100, 20, and 4 to 5, respectively. The separation factor, although not large, is sufficient for a chromatographic technique. This separation is impossible in aqueous hydrochloric acid because all of these elements fall in the non-adsorbable group. Manganese(II) could also be added to this group and be separated. Its distribution value is 1000 in the 95 percent ethyl alcohol-0.3 M hydrochloric acid eluting medium. However, preliminary experiments in this type of separation indicated considerable tailing.

The desorption effect of perchloric acid was used to try to eliminate the tailing. Elution curves were determined for nickel(II) in 95 percent ethyl alcohol-0.3 M hydrochloric acid with added perchloric acid (0.001 M, 0.01 M, 0.05 M, and 0.1 M). It was observed that as the perchloric acid concentration was increased, the major portion of the nickel(II) was eluted faster. The tailing also diminished, but not enough to be useful as part of the eluting medium.

Several other metals fit into this elution scheme even though their distribution coefficients were not determined. Comparison of these data to those found in aqueous hydrochloric acid by Kraus (39) leads to this conclusion. For example, the rest of the alkaline earths would probably exhibit similar adsorption as does calcium(II). Thallium(III), mercury(II), gold(III), and platinium metals would be similar to bismuth(III), germanium(IV) to cobalt(II), and gallium(III) to iron(III). However, it should be kept in mind that these are only qualitative conclusions and should be treated as such.

Although nickel(II) can be separated from cobalt(II) or manganese(II), tailing as well as broad elution bands does occur. It would be a distinct advantage to eliminate this in the separation. The 55 percent isopropyl alcohol with varying hydrochloric acid eluting scheme does just this. In Figure 29 nickel(II)-cobalt(II) elution curves of the two elution schemes are compared. In the ethyl alcohol elution 82 percent ethyl alcohol-0.3 M hydrochloric acid was continued after elution of nickel(II) until the cobalt(II) broke through. In the isopropyl alcohol elution 3 M hydrochloric acid-55 percent isopropyl alcohol was discontinued shortly after the elution of the nickel(II). The cobalt(II) band was still 4 cm. from the bottom of the resin column. Thus the cobalt(II) breakthrough would probably occur at about 250 ml. of the 3 M eluting agent. The nickel(II) band is much sharper and there is considerably less tailing in the isopropyl alcohol eluting medium. A better separation factor is also indicated for the isopropyl alcohol system. It should be noticed that a wider column was used in these latter separations as compared to those in Table 17. This allows greater loading with this larger cross-sectional area. However, larger volumes of eluting agent are necessary for the separation.

The isopropyl alcohol system (Figure 8 and 9) did not offer a convenient separation of nickel(II)-manganese(II)-cobalt (II). However, it is probable that a chromatographic technique could be used for the separation. Nickel(II) would be eluted with 4 M hydrochloric acid-55 percent isopropyl alcohol, manganese with 3 M hydrochloric acid-55 percent iso-propyl alcohol and cobalt(II) with 1.3 M hydrochloric acid-55 percent isopropyl alcohol. A disadvantage of this scheme is the high viscosity of the 3 and 4 M acid eluting medium. This causes very slow flow rates, particularly in the 4 M eluting agent. Upon examination of Figure 13 it became apparent that nickel (II) could be separated from manganese(II) by using 96 percent methyl alcohol-0.2 M hydrochloric acid. Nickel(II) and manganese(II) have distribution coefficient values in this medium of 0 and 27, respectively. To test this separation the elution curve of a nickel(II)-manganese(II) mixture was determined and is reproduced in Figure 30. The curve shows sharp bands with very little tailing and an excellent separation factor.

Elution curves for cobalt(II)-copper(II), manganese(II)-copper(II), and nickel(II)-cobalt(II)-copper(II)-zinc(II mixtures were also determined using the isopropyl alcohol eluting scheme. Again, sharp bands with very little tailing and excellent separation factors were obtained. The curve for the four component mixture, which is very similar to the others, is given in Figure 31.

Separation of several mixtures, 1:1 by weight, using this elution scheme are given in Table 18. Dowex 1 X8, 200 to 400 mesh, chloride form resin with a flow rate of 0.25 to 0.33 ml./min. was used. Column dimensions are given in parenthesis in the Table and the volume of wash solution is included with the first eluted metal ion. The order of the metal ions is the order of elution. The latter of the two sampling techniques was used in these separations.

The usual approach to ion exchange separations is to take up the minor constituent and elute the major constituent. In this manner the constituents can be concentrated and the analysis is thus less difficult. Also, in many cases, small columns are all that are necessary for the separation. It would appear that no difficulty would be encountered in the use of the proposed method for this type of separation. Table 19 contains some typical separations of this type. The ratios, by weight, are about 10 to 1. Eluting agents (not given in Table 19) are similar to the ones used in the separations listed in Table 18. The quantities are about the same except in the case of the elution of the major constituent where an additional 10 to 15 ml. of eluting agent was used. Similar flow rates were used. In all cases, the columns were 5 x 2.2 cm. and the resin was the Dowex 1 X8, 200 to 400 mesh, chloride form resin.

The measurement of distribution coefficients in mixed organic solvents (see Figure 26 and 27) offers a route to separation of the metal ions which are in the nonadsorbable group in aqueous hydrochloric acid. The methyl alcohol-ethyl alcohol eluting medium appears to have better separation factors than the methyl alcohol-isopropyl alcohol eluting medium. The possibility of separation of a nickel(II), rare earth(III), and thorium(IV) mixture, which cannot be done in aqueous hydrochloric acid, was tested using the elution scheme suggested by the distribution data. Composition of the eluting agents used were, for nickel(II), 23 percent methyl alcohol-73 percent ethyl alcohol-0.2 M hydrochloric acid, for dysprosium(III), 52 percent methyl alcohol-44 percent ethyl alcohol-0.2 M hydrochloric acid, and for thorium(IV), 96 percent methyl alcohol-0.2 M hydrochloric acid. Naturally, for a separation of nickel(II) from thorium(IV), an eluting agent containing more methyl alcohol would be used. Elution curves were determined on a 6 X 2.2 cm. column of Dowex 1 X8, 200 to 400 mesh, chloride form resin. Considerable tailing was observed, particularly in the case of nickel(II). Thus the separation of nickel(II) and dysprosium(III) is not very satisfactory. However, it appeared that nickel(II)-thorium (IV) and dysprosium(III)-thorium(IV) mixtures could be separated. The methyl alcohol eluting agent for thorium(IV) is not ideal because thorium(IV) has a D value of about 2 in this medium. This is partly responsible for the tailing in the thorium(IV) elution.

The selection of the medium for elution, in all cases, depends on whether further separations are to be made. If no other metal ions are to be separated thorium(IV) could be eluted easily with aqueous hydrochloric acid. However, if manganese(II) is present the methyl alcohol eluting agent would be used. In this manner, thorium(IV) can be separated from manganese(II). An example of this separation is given in Table 18. It must be emphasized that to obtain quantitative separations using the methyl alcohol-ethyl alcohol eluting medium where tailing is a characteristic, extreme care should be used in selecting proper volumes for complete separation.

To simplify the selection of conditions for separation, the distribution data are summarized in Table 20. The metal ions are listed in probable order of elution after adsorption from 95 percent ethyl alcohol-0.3 M hydrochloric acid. In several instances alternate eluting agents are available and can be interchanged without any loss in efficiency in the separation. Several separations suggested in the Table have not been proven, experimently, to be quantitative (compare to previous Tables of separations). However, from a purification point of view, where quantitative results are not required, these separations are of practical value. Also, as previously stated, many more metal ions will fit into this scheme.

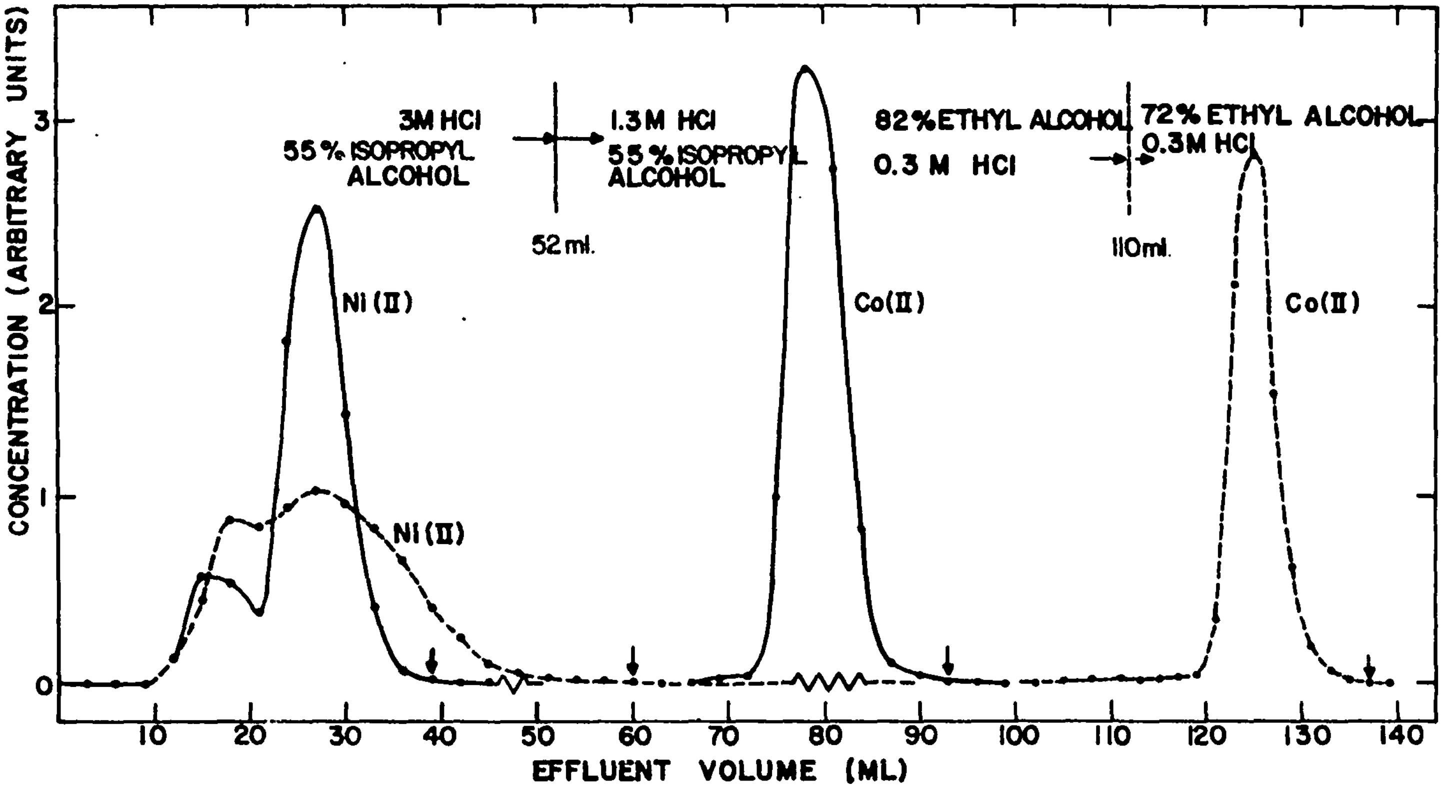

Figure 29. Comparison of the isopropyl alcohol (solid line) and the ethyl alcohol (dotted line) elution schemes for a cobalt(II)-nickel(II) separation. A 5 X 2.2 cm. column of Dowex 1 X8, 200 to 400 mesh, chloride form resin and a flow rate of 0.25 to 0.33 ml./min. used for the separation. Arrow signifies the fraction containing the last detectable trace of the metal ion

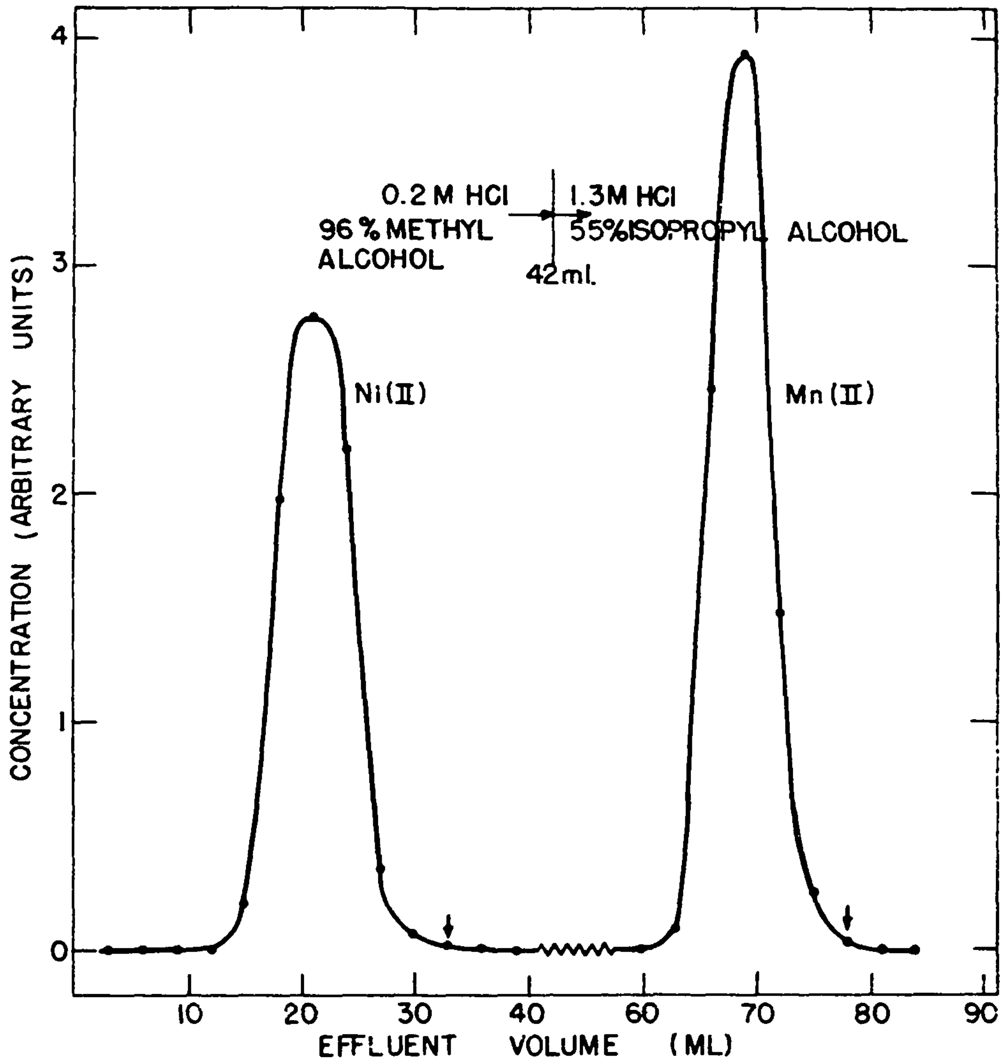

Figure 30. Elution curve for the separation of a nickel(II)-manganese(II) mixture. A 6 x 2.2 cm. column of Dowex 1 X8, 200 to 400 mesh, chloride form resin and a flow rate of 0.25 to 0.33 ml/min. used for the separation. Arrow signifies the fraction containing the last detectable trace of the metal ion

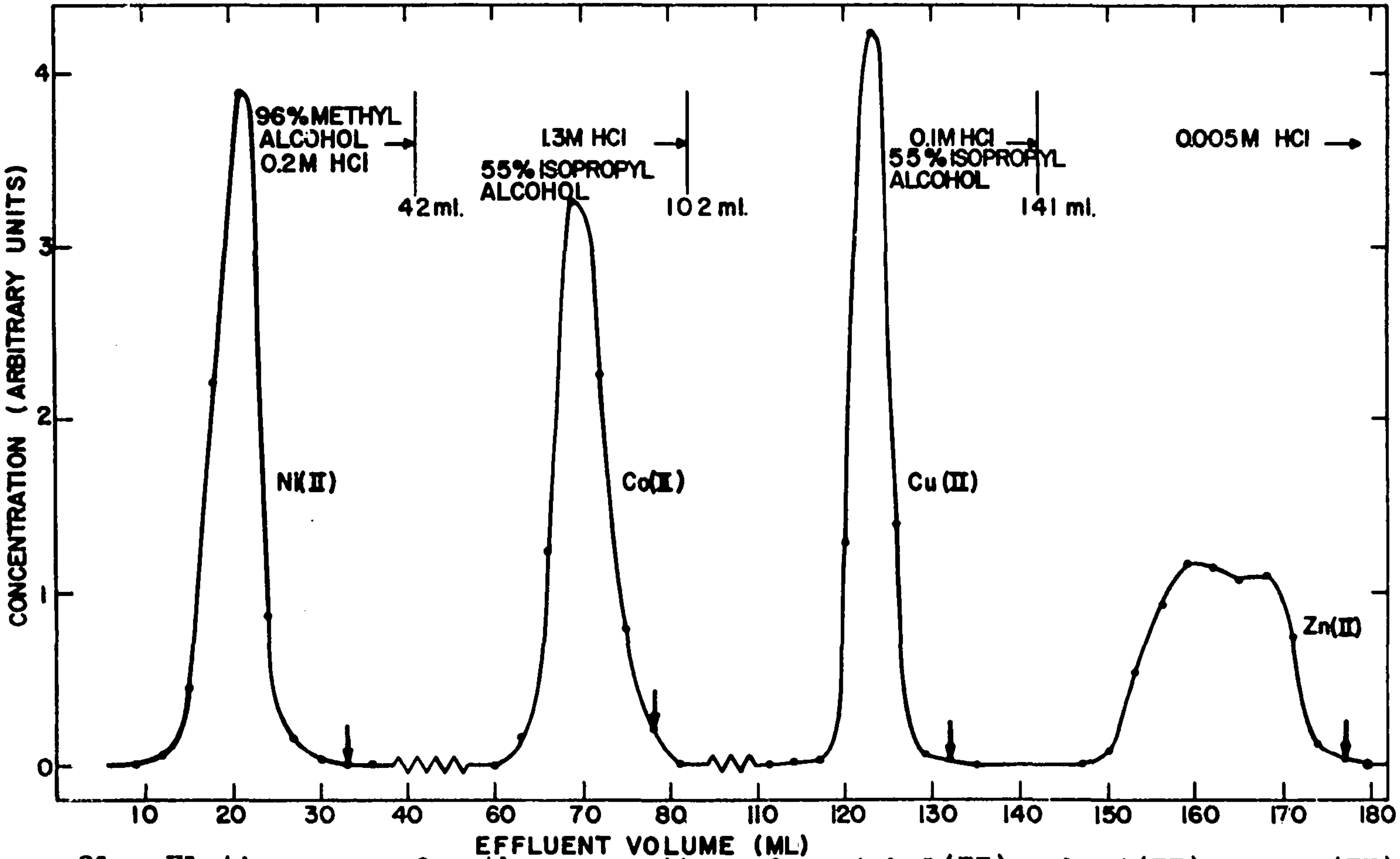

Figure 31. Elution curve for the separation of a nickel(II)-cobalt(II)-copper(II)-zinc(II) mixture. A 6 x 2.2 cm. column of Dowex 1 X8, 200 to 400 mesh, chloride form resin and a flow rate of 0.25 to 0.33 ml./min. used for the separation. Arrow signifies the fraction containing the last detectable trace of the metal ion

Table 17. Separation and analysis of synthetic metal ion mixtures

| Metal mixtures (sample size and column dimensions) | | | |
|---|---|---|---|
| | Eluting agent[a] | Mg. taken | Mg. found |
| Ni(II)-Cu(II) (4 ml., 3 x 1.1 cm.) | | | |
| Ni | 2 ml. 95% EtOH-0.3 M HCl | | |
| | 10 ml. 74% EtOH-0.3 M HCl | 7.17 | 7.17 |
| Cu | 15 ml. 40% EtOH-0.3 M HCl | 7.08 | 7.01 |
| Ni(II)-Cu(II)-Zn(II) (4 ml., 3 x 1.1 cm.) | | | |
| Ni | 2 ml. 95% EtOH-0.3 M HCl | | |
| | 9 ml. 74% EtOH-0.3 M HCl | 7.17 | 7.17 |
| Cu | 15 ml. 40% EtOH-0.3 M HCl | 7.08 | 7.02 |
| Zn | 40 ml. 0.005 M aqueous HCl | 7.15 | 7.16 |
| Mn(II)-Cu(II) (4 ml., 3 x 1.1 cm.) | | | |
| Mn | 2 ml. 95% EtOH-0.3 M HCl | | |
| | 11 ml. 74% EtOH-0.3 M HCl | 7.16 | 7.13 |
| Cu | 15 ml. 40% EtOH-0.3 M HCl | 7.08 | 7.02 |
| Ni(II)-Mn(II)-Cu(II) (4 ml., 3 x 1.1 cm.) | | | |
| Ni | 2 ml. 95% EtOH-0.3 M HCl | | |
| | 41 ml. 95% EtOH-0.3 M HCl | 7.17 | 7.11 |
| Mn | 10 ml. 72% EtOH-0.3 M HCl | 7.16 | 7.12 |
| Cu | 25 ml. 0.005 M aqueous HCl | 7.08 | 7.02 |
| Ni(II)-Co(II)-Cu(II)-Zn(II) (4 ml., 6 x 1.1 cm.) | | | |
| Ni | 2 ml. 95% EtOH-0.3 M HCl | | |
| | 12 ml. 82% EtOH-0.3 M HCl | 7.17 | 7.10 |
| Co | 17 ml. 72% EtOH-0.3 M HCl | 7.64 | 7.62 |
| Cu | 15 ml. 40% EtOH-0.3 M HCl | 7.08 | 7.04 |
| Zn | 40 ml. 0.005 M aqueous HCl | 7.15 | 7.20 |

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[a] EtOH = ethyl alcohol

Table 17. (Continued)

| Metal mixtures (sample size and column dimensions) | Eluting agent[a] | Mg. taken | Mg. found |
|---|---|---|---|
| Ni(II)-Co(II) (4 ml., 6 x 1.1 cm.) | | | |
| Ni | 2 ml. 95% EtOH-0.3 M HCl | | |
| | 13 ml. 82% EtOH-0.3 M HCl | 7.17 | 7.23 |
| Co | 15 ml. 40% EtOH-0.3 M HCl | 7.64 | 7.62 |
| Co(II)-Fe(III) (4 ml., 3 x 1.1 cm.) | | | |
| Co | 2 ml. 95% EtOH-0.3 M HCl | | |
| | 10 ml. 72% EtOH-0.3 M HCl | 7.64 | 7.62 |
| Fe | 23 ml. 40% EtOH-0.3 M HCl | 6.90 | 6.92 |
| Ni(II)-Co(II)-Fe(III)-Zn(II) (4 ml., 6 x 1.1 cm.) | | | |
| Ni | 2 ml. 95% EtOH-0.3 M HCl | | |
| | 13 ml. 82% EtOH-0.3 M HCl | 7.17 | 7.21 |
| Co | 15 ml. 70% EtOH-0.3 M HCl | 7.60 | 7.63 |
| Fe | 20 ml. 40% EtOH-0.3 M HCl | 6.90 | 6.90 |
| Zn | 40 ml. 0.005 M aqueous HCl | 6.91 | 6.82 |
| Ni(II)-Fe(III)-Bi(III) (4 ml., 3 x 1.1 cm.) | | | |
| Ni | 2 ml. 95% EtOH-0.3 M HCl | | |
| | 6 ml. 72% EtOH-0.3 M HCl | 7.17 | 7.17 |
| Fe | 12 ml. 40% EtOH-0.3 M HCl | 6.90 | 6.88 |
| Bi | 25 ml. 1 M aqueous $H_2SO_4$ | 6.91 | 6.82 |

Table 18. Separation and analysis of synthetic metal ion mixtures

| Metal mixture (column dimensions) | Eluting agent$^{a,b,c}$ | Mg. taken | Mg. found |
|---|---|---|---|
| Ni(II)-Fe(III)-Bi(III) (6 x 2.2 cm. | | | |
| Ni | 4 ml. 95% EtOH-0.3 M HCl | | |
| | 50 ml. 96% MeOH-0.2 M HCl | 8.96 | 8.93 |
| Fe | 45 ml. 0.1 M HCl-55% 2-PrOH | 9.13 | 9.13 |
| Bi | 90 ml. 1 M aqueous $H_2SO_4$ | 8.67 | 8.50 |
| Co(II)-Fe(III) (6 x 2.2 cm.) | | | |
| Co | 4 ml. 95% EtOH-0.3 M HCl | | |
| | 60 ml. 1.3 M HCl-55% 2-PrOH | 9.52 | 9.59 |
| Fe | 45 ml. 0.1 M HCl-55% 2-PrOH | 9.13 | 9.12 |
| Ni(II)-Mn(II)-Cu(II) (6 x 2.2 cm. | | | |
| Ni | 8 ml. 95% EtOH-0.3 M HCl | | |
| | 47 ml. 96% MeOH-0.2 M HCl | 8.96 | 8.94 |
| Mn | 80 ml. 3 M HCl-55% 2-PrOH | 8.96 | 9.00 |
| Cu | 50 ml. 0.1 M HCl-55% 2-PrOH | 8.95 | 8.90 |
| Ni(II)-Mn(II)-Co(II)-Cu(II)-Zn(II) (6 x 2.2 cm. | | | |
| Ni | 8 ml. 95% EtOH-0.3 M HCl | | |
| | 47 ml. 96% MeOH-0.2 M HCl | 8.96 | 8.99 |
| Mn | 80 ml. 3 M HCl-55% 2-PrOH | 8.96 | 8.88 |
| Co | 70 ml. 1.3 M HCl-55% 2-PrOH | 9.52 | 9.51 |
| Cu | 50 ml. 0.1 M HCl-55% 2-PrOH | 8.95 | 8.89 |
| Zn | 60 ml. 0.005 M aqueous HCl | 8.95 | 9.06 |

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[a] EtOH = ethyl alcohol

[b] MeOH = methyl alcohol

[c] 2-PrOH = isopropyl alcohol

Table 18. (Continued)

| | Metal mixture (column dimensions) Eluting | Mg. taken | Mg. found |
|---|---|---|---|
| Ni(II)-Co(II)-Cu(II)-Bi(III) (6 x 2.2) | | | |
| Ni | 8 ml. 95% EtOH-0.3 M HCl | | |
| | 47 ml. 96% MeOH-0.2 M HCl | 8.96 | 9.06 |
| Co | 65 ml. 1.3 M HCl-55% 2-PrOH | 9.52 | 9.52 |
| Cu | 40 ml. 0.1 M HCl-55% 2-PrOH | 8.95 | 8.98 |
| Bi | 85 ml. 1 M aqueous $H_2SO_4$ | 8.67 | 8.54 |
| Dy(III)-Mn(II)-Cu(II)-Fe(III)-Bi(III) (6 x 2.2 cm.) | | | |
| Dy | 8 ml. 95% EtOH-0.3 M HCl | | |
| | 47 ml. 96% MeOH-0.2 M HCl | 9.22 | 9.28 |
| Mn | 80 ml. 3 M HCl-55% 2-PrOH | 8.96 | 8.99 |
| Cu-Fe[d] | 50 ml. 0.1 M HCl-55% 2-PrOH | | |
| | Cu | 8.95 | 9.01 |
| | Fe | 9.13 | 9.06 |
| Bi | 85 ml. 1 M aqueous $H_2SO_4$ | 8.67 | 8.67 |
| Ni(II)-Th(IV)-Mn(II)-Co(II)-Cu(II)-Fe(III) (6 x 2.2 cm.) | | | |
| Ni | 8 ml. 95% EtOH-0.3 M HCl | | |
| | 73 ml. 48% EtOH-48% MeOH-0.2 M HCl | 8.96 | 9.00 |
| Th | 85 ml. 96% MeOH-0.2 M HCl | 9.07 | 9.07 |
| Mn | 85 ml. 3 M HCl-55% 2-PrOH | 8.96 | 8.97 |
| Co | 55 ml. 1.3 M HCl-55% 2-PrOH | 9.52 | 9.57 |
| Cu-Fe[d] | 50 ml. 0.1 M HCl-55% 2-PrOH | | |
| | Cu | 8.95 | 8.97 |
| | Fe | 9.13 | 9.04 |
| Ca(II)-Mn(II) (5 x 2.2 cm.) | | | |
| Ca | 2 ml. 95% EtOH-0.3 M HCl | | |
| | 56 ml. 96% MeOH-0.2 M HCl | 8.34 | 8.41 |
| Mn | 80 ml. 3 M HCl-55% 2-PrOH | 9.06 | 9.02 |
| Ni(II)-Mn(II) (5 x 2.2 cm.) | | | |
| Ni | 2 ml. 95% EtOH-0.3 M HCl | | |
| | 56 ml. 96% MeOH-0.2 M HCl | 4.45 | 4.51 |
| Mn | 80 ml. 3 M HCl-55% 2-PrOH | 9.06 | 9.07 |

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[d] Cu-Fe eluted together and analyzed by a photometric titration (127) with EDTA as titrant

Table 19. Separation and analysis of synthetic metal ion mixtures. Column dimensions-5 x 2.2 cm

| Metal Mixture | | Mg. taken | Mg. found |
|---|---|---|---|
| Co(II)-Cu(II) | | | |
| | Co | 38.46 | 38.40 |
| | Cu | 4.467 | 4.455 |
| Ni(II)-Co(II) | | | |
| | Ni | 35.46 | 35.48 |
| | Co | 4.822 | 4.817 |
| Co(II)-Fe(III) | | | |
| | Co | 38.46 | 38.49 |
| | Fe | 4.633 | 4.644 |
| Mn(II)-Co(II) | | | |
| | Mn | 36.22 | 36.39 |
| | Co | 4.822 | 4.828 |
| Ca(II)-Mn(II) | | | |
| | Ca | 33.34 | 33.36 |
| | Mn | 4.510 | 4.599 |
| Ni(II-Mn(II) | | | |
| | Ni | 35.46 | 35.55 |
| | Mn | 4.510 | 4.654 |

Table 20. Approximate elution order of metal ions

| Eluting agent | Metals retained | Metals eluted[a] |
|---|---|---|
| 60% methyl alcohol-40% ethyl alcohol-0.2 M HCl | Th$^{4}$, Mn$^{2}$, Co$^{2}$, Cu$^{2}$, Fe$^{3}$, UO$_2^{2}$, Zn$^{2}$, Cd$^{2}$, Bi$^{3}$ | R. E.$^{3}$, Ni$^{2}$, Ca$^{2}$, (VO$^{2}$, Cr$^{3}$, Sc$^{3}$) |
| 96% methyl alcohol-0.2 M HCl | Mn$^{2}$, Co$^{2}$, Cu$^{2}$, Fe$^{3}$, UO$_2^{2}$, Zn$^{2}$, Cd$^{2}$, Bi$^{3}$ | Th$^{4}$, R. E.$^{3}$, Ni$^{2}$, Ca$^{2}$, VO$^{2}$, Cr$^{3}$, Sc$^{3}$ |
| 95% ethyl alcohol-0.3 M HCl | Mn$^{2}$, Co$^{2}$, Cu$^{2}$, Fe$^{3}$, UO$_2^{2}$, Zn$^{2}$, Cd$^{2}$, Bi$^{3}$ | Chromatographic order of elution<br>1. Ni$^{2}$, Ca$^{2}$, VO$^{2}$, Cr$^{3}$<br>2. R. E.$^{3}$ , Sc$^{3}$<br>3. Th$^{4}$ |
| 82% ethyl alcohol-0.3 M HCl | Co$^{2}$, Cu$^{2}$, Fe$^{3}$, UO$_2^{2}$, Zn$^{2}$, Cd$^{2}$, Bi$^{3}$ | Ni$^{2}$, Ca$^{2}$, VO$^{2}$, Cr$^{3}$, R. E.$^{3}$, Th$^{4}$, (Mn$^{2}$) |
| 3 M HCl-55% isopropyl alcohol | Co$^{2}$, Cu$^{2}$, Fe$^{3}$, UO$_2^{2}$, Zn$^{2}$, Cd$^{2}$, Bi$^{3}$ | Ni$^{2}$, Ca$^{2}$, VO$^{2}$, Cr$^{3}$, R. E.$^{3}$, Th$^{4}$, Mn$^{2}$ |
| 1.3 M HCl-55% isopropyl alcohol | Cu$^{2}$, Fe$^{3}$, UO$_2^{2}$, Zn$^{2}$, Cd$^{2}$, Bi$^{3}$ | Co$^{2}$, all previous metals |

[a] Metals in parentheses are partially eluted

Table 20. (Continued)

| Eluting agent | Metals retained | Metals eluted |
|---|---|---|
| 72% ethyl alcohol-0.3 M HCl | $Cu^2$, $Fe^3$, $UO_2^2$, $Zn^2$ $Cd^2$, $Bi^3$ | $Co^2$, all previous metals |
| 0.1 M HCl-55% isopropyl alcohol | $Zn^2$, $Cd^2$, $Bi^3$ | $Cu^2$, $Fe^3$, $UO_2^2$, all previous metals |
| 40% ethyl alcohol-0.3 M HCl | $Zn^2$, $Cd^2$, $Bi^3$ | $Cu^2$, $Fe^3$, $UO_2^2$, all previous metals |
| 0.005 M aqueous HCl | $Bi^3$ | $Zn^2$, $Cd^2$, all previous metals |
| 1 M $H_2SO_4$ | | $Bi^3$, all previous metals |

## SUMMARY

A systematic approach to anion exchange in partially nonaqueous solvents was initiated. Distribution coefficients of metal ions for Dowex 1 X8, chloride form resin in organic solvent-water mixtures containing hydrochloric acid were measured. The organic solvents used were methyl alcohol, ethyl alcohol, isopropyl alcohol, acetone, and dioxane.

When the organic solvent concentration is increased and the hydrochloric acid concentration is held constant, the distribution coefficient will increase. Similarly, if the hydrochloric acid concentration is increased while holding the organic solvent concentration constant, the distribution coefficient will increase. The order of the distribution coefficients in the alcoholic-acid-water mixtures was found to be: isopropyl > ethyl > methyl alcohol.

In many cases, distribution coefficients were found to be significantly higher than in water-hydrochloric acid systems. Several metal ions [thorium(IV), nickel(II), calcium (II), rare earths(III), chromium(III), and vanadyl(IV)] which do not adsorb in aqueous hydrochloric acid were found to be adsorbed when an organic solvent is present.

Three elution schemes for metal ion separations were proposed. In the first scheme the eluting agents contain 0.3 M hydrochloric acid with varying percent of ethyl alcohol. The

eluting agents in the second scheme contain 55 percent isopropyl alcohol with varying concentrations of hydrochloric acid. The last scheme contains 0.2 M hydrochloric acid and a mixture of methyl and ethyl alcohol totaling 96 percent. Successful separations of a number of metal ion mixtures were performed using these elution schemes.

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