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CATION-EXCHANGE BEHAVIOR OF DI-,
TRI-, AND TETRAVALENT METAL IONS IN
ETHYLENEDIAMMONIUM SALT SOLUTIONS

by

Richard Thornton Oliver

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

Major Subject: Analytical Chemistry

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INTRODUCTION

In the course of investigating the separation of metal ions by ion-exchange chromatography it was found that cations of different charge magnitude could be separated simply and quickly on a cation-exchange column using a solution of an ethylenediammonium salt as the eluting agent (28). The use of the ethylenediammonium ion, a divalent ion, permits the elution of a given ion at lower eluant concentrations than is possible with an acid or other monovalent eluant. The analysis of the metal ion contained in the effluent is normally not hindered by the presence of ethylenediammine or its acid salts, whereas most other divalent ions would interfere. Also, the adjustment of effluent pH is facilitated because a large volume of acid is not present to be neutralized.

The development of separation procedures by ion-exchange chromatography is normally a trial and error process. Before the optimum conditions are determined, several single-element elutions, using different concentrations of eluant, must be performed. It was of interest to evaluate ion-exchange separations by chromatographic elution with ethylenediammonium salts using a minimum of experimental data. The aim of this thesis is to measure the distribution coefficients of a number of metal ions in ethylenediammonium salt solutions and thus predict the conditions for column separations. From a plot of the distribution coefficients vs. the eluant concentration for

each metal, the separation of any two curves, at a particular eluant concentration, is a measure of the selectivity coefficient for the respective metal ions. The actual selectivity coefficient may be obtained by the ratio of the distribution coefficients taken from the curves at that point. The most obvious choice of eluant concentration is where the ratio of the distribution coefficients is the greatest. Although this concentration may give the best theoretical separation, the distribution coefficients of the individual species can be so great that the time needed for elution would be impractical. In most cases, a lower selectivity coefficient can be selected while still achieving a quick, efficient separation.

Previous column work indicated the importance of several variables on the elution of metal ions: (1) The anion associated with the ethylenediammonium ion; (2) temperature; and (3) the initial metal ion concentration. Because the elution behavior of ions is related to their respective distribution coefficients, the measurement of batch equilibrium distribution coefficients offers a simple and convenient method of studying these variables. The distribution coefficients of some tri- and tetravalent cations were measured in ethylenediammonium chloride solutions as well as in ethylenediammonium perchlorate. Some di-, tri-, and tetravalent cations were studied in 0.2 M ethylenediammonium perchlorate as a function of temperature and also as a function of initial metal ion concentration. All variables caused a change in the distribution coefficients, the

magnitude of which increased with increasing charge on the metal ion.

Distribution coefficient data for polyvalent cations are not generally available in the literature. Bonner et al. (7, 10) have reported a thermodynamic selectivity scale of mono-, di-, and some trivalent ions based on the exchange on the lithium form of Dowex-50. Others (23, 72), have studied the distribution of fission products between an aqueous acid phase and Dowex-50. Distribution data serve a two-fold purpose to the chemist. The first is theoretical. Measurement of distribution coefficients has shed light on complex formation using 5f orbitals in the actinide elements (23); heats of reactions for ion-exchange reactions have been determined (45, 46); and insight into the mechanics of ion-exchange processes can be obtained (22). The second use is in determining selectivity coefficients for chromatographic exchanges. The distribution coefficients for the rare earth elements on a cation-exchange resin are very similar and separations are therefore difficult using non-complexing eluting agents. However, if a complexing agent, such as citrate, is used to elute the rare earths, a second factor, the complexing of the rare earths, must be considered in the distribution coefficient expression. (See page 37 for a discussion of the effect of complexing agents on the distribution coefficients.) The selectivity coefficient of, for example, cerium and yttrium in citrate solutions, may be defined as the ratio of the distribution coefficients, \underline{D}_O , and can be shown to

be equal to

$$K = \frac{D_o^{Ce}}{D_o^Y} = \left(\frac{D^{Ce}}{D^Y} \right) \left(\frac{K_{comp}^Y}{K_{comp}^{Ce}} \right) \quad (1)$$

where \underline{D} is the distribution coefficient in the absence of citrate, and \underline{K}_{comp} is the stability constant for the rare earth-citrate complex. The ratio of the distribution coefficients for cerium and yttrium in the absence of complexing has a value of 1.55 and the ratio of the complex stability constants 2.9 (38). It is obvious that the role of the citrate is to increase the separation coefficient and thus achieve a better separation of cerium and yttrium. From a measurement of the distribution coefficient of ions in the absence of complexing agents and the stability constants of metal complexes, the selectivity coefficient can be calculated. For acid ligands, the stability constants are dependent upon pH.

Fritz and Umbreit (31) used this acid dependence of stability constants to determine the pH at which the EDTA complex of one metal will be dissociated, and the metal taken up by a cation resin, while the EDTA complex of a second metal is undissociated and passes through the resin. The pH at which a metal complex dissociates can be calculated from the formation constant of the complex, from the acid dissociation constants of the complexing agent, and from the distribution coefficient of the metal ion between the resin and the aqueous phase. Excellent pH control is effected by using a buffer in the sample

and equilibrating the resin with the same buffer prior to passage of the sample through it.

REVIEW OF LITERATURE

Because this thesis is primarily concerned with ion-exchange equilibria, descriptive material in the use and kinetics of ion-exchange resins will be omitted. Complete technical data and a good introduction to the kinetics and thermodynamic properties of ion exchangers may be found in recent publications (25, 40, 49). The subject of chromatographic separations using both anion and cation resins was reviewed by Schindewolf (64) in 1957. Following a short summary of ion-exchange separations he tabulates separations reported in the literature by periodic groups, giving the resin used, the eluant, and the reference. Kunin et al. (48) brought the literature up to date in 1958. Oliver and Fritz (53) reviewed the single-pass and chromatographic methods of separation. More detailed discussions of ion-exchange processes may be found in books written on the subject (17, 40, 47, 57).

Probably the first systematic study of the behavior of metal ions on an ion-exchange resin was done by Kraus and his associates (43). They found that the strong-base anion-exchange resins show great selectivities for the chloride complexes of a number of metals. An anion-exchange column was loaded with tracer amounts of the metal ion and eluted with hydrochloric acid solutions of 0.1 to 12 M. The movement of the band was described in terms of an elution constant E:

$$E = dA/V \quad (2)$$

where \underline{d} is the distance moved by the band, \underline{A} is the cross-sectional area of the column and \underline{V} is the volume of eluant passed through the column (42). If correction is made for the void space between the particles of resin the experimentally determined \underline{E} may be related to the column distribution coefficient, \underline{C} :

$$E = 1/(C + i) \quad (3)$$

where \underline{i} is the void fraction of the column. Kraus plotted $\log \underline{C}$ vs. concentration of hydrochloric acid for each of the elements studied. These curves are very useful in the field of analytical separations. A quick glance at them will show whether there is a possibility of separating two metal ions by anion-exchange chromatography using hydrochloric acid as eluant.

Bunney et al. (14) extended the work of Kraus to include measurements of distribution coefficients in nitric and sulfuric acids. A log-log plot of the distribution coefficient vs. the acid concentration for each metal showed the possibility of many interesting separations. Thorium, protactinium, uranium, and zirconium are taken up by Dowex-2 from 0.1 N sulfuric acid while americium is not. Rare earths can be separated from thorium, protactinium, uranium, zirconium, niobium, molybdenum, and ruthenium by a similar procedure. Cabell and Milner (16) were able to separate tantalum and niobium and Danon (20) separated thorium from rare earths by anion-exchange chromatography. Preliminary distribution coefficients were measured in several eluant solutions to evaluate conditions

giving the best selectivity coefficients prior to column runs. Freiling et al. (26) extended Bunney's work by studying the adsorption of metal ions on an anion resin as a function of phosphoric acid concentration. Wish (72) studied the anion exchange behavior of some metal ions in mixed acid (HCl-HF) solutions and developed a separation scheme from distribution coefficient vs. acid concentration plots. Kraus et al. (43) also carried out some investigations in mixed acid solutions. Stewart (68) reported selectivity coefficients for rare earth and transplutonium elements calculated from elution curves using buffered glycolic acid as eluant. He also reports selectivity coefficients derived from the literature in an attempt to compare the efficiencies of various eluants on the separation of these elements. Berman and McBryde (3) studied the platinum metals in a similar manner.

Distribution studies have not been limited to anion exchange studies. An extensive study has been made by Bonner and co-workers concerning ion-exchange equilibria on Dowex-50. During the past six years, considerable data have been published on the exchange of metals of equal charge (6, 7, 8, 9, 10) and of unequal charge (7, 8, 10) for mono-, di-, and trivalent metal ions. The purpose of his investigations was to "collect exact cation-exchange equilibria data...for a thoroughly characterized resin" (9). Equilibria were measured by the batch procedure and equilibrium quotients calculated. The equilibrium quotients were plotted as a function of mole-percent resin and

reported as such. True thermodynamic equilibrium constants, \underline{K}_a , were then calculated from the following equation:

$$\log K_a = \int_0^1 (\log K) dN \quad (4)$$

\underline{K} being the equilibrium quotient corrected for solution activities and \underline{N} the mole fraction of the resin. The integration was carried out graphically on plots of $\log \underline{K}$ vs. \underline{N} .

A selectivity scale (based on the above \underline{K}_a values) for mono-, di-, and trivalent cations on Dowex-50 was prepared (7, 9). This scale is extremely helpful in determining the affinity of metals for the ion-exchange resin at unit activity (all measurements were made at unit activity). It also represents quantitative evidence supporting the well-known experimentally observed fact that ions of greater charge are more strongly adsorbed than those of lesser charge. The order of selectivity for a resin is subject to variation depending upon several variables, not all of which may be known (12). Some of the known variables are the capacity of the resin, the cross linkage, and the percentage of each ion associated with the resin. These points are considered in Bonner's study. Other known variables such as solution composition (chelating or complexing agents present) and concentration of separable ions, both of major importance to the analytical chemist, are not covered by Bonner. Therefore his data are of limited practical importance for actual analytical separations by ion-exchange chromatography.

During an investigation into the similarities between the lanthanides and actinides, Diamond et al. (23) studied the elution behavior of members of these groups plus the alkaline earth metals with various concentrations of hydrochloric acid from Dowex-50 cation-resin columns. Much of this work was confirmed by batch-wise measurements of the distribution coefficients. Diamond (22) furthered this work and included the alkali metals. These authors were more concerned with the factors influencing ion-exchange equilibria and explaining the results than with analytical separations. However, their data indicate that separations of the alkali metals, the alkaline earth metals, or mixtures of the two groups can be obtained by eluting the ions from Dowex-50 with 1 to 5 M hydrochloric acid. Lithium, sodium, and potassium have separated using 0.7 M HCl (70). The separation of cesium and rubidium using 0.2 M hydrochloric acid and of calcium from strontium using 1 M hydrochloric acid have also been reported (61).

Cabell (15) separated mono-, di-, and trivalent impurities (strontium being the major impurity) from pile-irradiated calcium using Zeokarb-225. A batch-type study of the distribution coefficient vs. hydrochloric acid concentrations preceded column separations. Hettel (35) separated a rare earth-thorium-common element mixture by chromatographic elution from Dowex-50 using 4 M hydrochloric acid. More recently, Strelow (69) separated thorium from zirconium and rare earths by eluting from Dowex-50 with 4 M hydrochloric acid. The conditions for

separation were evaluated from both distribution data and single-element elution curves. Belyavskaya and Chmutova (2) separated zirconium from chromium and aluminum by hydrochloric acid elution.

Rieman and co-workers separated mixtures by both anion and cation chromatography. They separated and analyzed the halide ions (21, 56), the lower condensed phosphates (ortho-, pyro-, tri-, trimeta-, and tetrametaphosphates) (5, 50, 54), and the major acids of fruits (malic, tartaric, and citric) (63) by anion-exchange chromatography. The alkali metals (4, 70) and the alkaline earth metals (49) were separated using cation-exchange chromatography. From single-component elution curves and equations relating the concentration of species in the effluent to the distribution ratio and volume of effluent at which the maximum amount of species exists (4, 55), the actual conditions to effect a quantitative separation were predicted with excellent accuracy. (An outline of the theory used is presented in the following section.) More recently Rieman and his group have directed their efforts toward a process for chromatographic separation of water-soluble non-electrolytes with exchange resins and aqueous salt solutions. This technique of "salting-out chromatography" has been applied to alcohols (62), amines (59), aliphatic and polyglycol ethers and carboxylic acids (60), aldehydes and ketones (13), and to the separation of phenols and alcohols (66). The conditions for the separations were found almost entirely by calculations based on the plate theory.

Sargent and Rieman (58, 61) studied the separation of glycols on the borate form of an anion-exchange resin by means of the plate theory.

An interesting application of the use of distribution studies in ion-exchange was recently reported by Kraus et al. (41). They observed distribution coefficients of greater than 10^5 for trace amounts of the anionic complexes MCl_4^{-1} of iron, gallium, and trivalent gold on Dowex-50, a cation resin, in concentrated chloride solutions. Under these same conditions the adsorption of anionic complexes of antimony (V) and thallium (III) was considerably less and that of manganese, cobalt, zinc, bismuth, and tin (IV) was negligible. From plots of the distribution coefficients vs. molality of chloride ion, separations of cesium from gold and tin (IV) and indium (III) from tin (IV) were predicted and actually carried out. No explanation for these phenomena was offered, but an interaction between the complexes and the organic network of the resin was mentioned.

Although many studies have been made of the ion-exchange behavior of metal ions, most of these have been conducted in a complexing medium. Separations performed in these media are based, to a large extent, on complex formation and not on the difference in affinity of the resin for species of different charge magnitude. Fritz and Karraker (28) separated divalent metal ions from trivalent metal ions on Dowex-50 X8 in the ethylenediammonium form by eluting with ethylenediammonium chloride. Their work is being continued and will include sep-

arations of trivalent metal ions from tetravalent metal ions
as well as complex mixtures.

THEORETICAL CONSIDERATIONS

Several attempts have been made to develop an adequate quantitative theory to describe the elution curves obtained in chromatographic work. The work of Rieman (4, 55) appears the most useful to the analytical chemist. Taking an approach similar to Martin and Synge (51) and Mayer and Tompkins (52) Rieman developed a simplified plate theory based on three assumptions: (1) the ion-exchange column consists of theoretical plates similar to a distillation column; (2) equilibrium must exist at all times during the elution; and (3) that the meq. of sample taken for elution is small in comparison to the concentration of eluant. The chromatographic elution is governed by the following equations:

$$U^* = V(D' + 1) \quad (5)$$

$$D' = \frac{EQW}{V\sqrt{El}^2} \quad (6)$$

$$\log M = \log M^* - 0.217 p \left(\frac{C + 1}{C} \right) \left(\frac{U + U^*}{U^*} \right)^2 \quad (7)$$

$$p = \left(\frac{2D'}{D' + 1} \right) \left(\frac{U^*}{U_a + U^*} \right) \quad (8)$$

where D' = distribution ratio = solute A in resin of any plate divided by solute A in solution phase of same plate.

E = equilibrium exchange constant.

El = chemical symbol for eluant.

M = concentration of solute A in any particular eluate fraction.

M^* = maximum concentration of M.

p = number of theoretical plates in a column.

Q = exchange capacity of resin, meq. per gram.

U = volume of eluant passed through column at any point of elution, ml.

$U^* = U$ when $M = M^*$.

$U_a = U$ when $M = M^*/e$.

$e = 2.72$ = base of natural logarithm.

V = interstitial volume of column, ml.

W = weight of resin, g.

z = valence of ion being chromatographed.

H = height of column, cm.

$P = p/H$ = the number of theoretical plates per cm.

The application of these equations may be illustrated with the aid of an example showing the separation of two solutes A and B. A typical result showing the concentration of each species in the solution leaving the column, M, as a function of total volume passed through the column, U, is shown in Figure 1. The overlap region between the two curves depends on: (1) the volume between the peak maxima ($\underline{U}_B^* - \underline{U}_A^*$) and (2) the shape and width of each peak (\underline{U}_a and \underline{M}^*/e). Equation 4 shows that the peak maximum, \underline{U}^* , is controlled by the distribution ratio \underline{D}' . Division of equation 5 for solute A by that for solute B gives

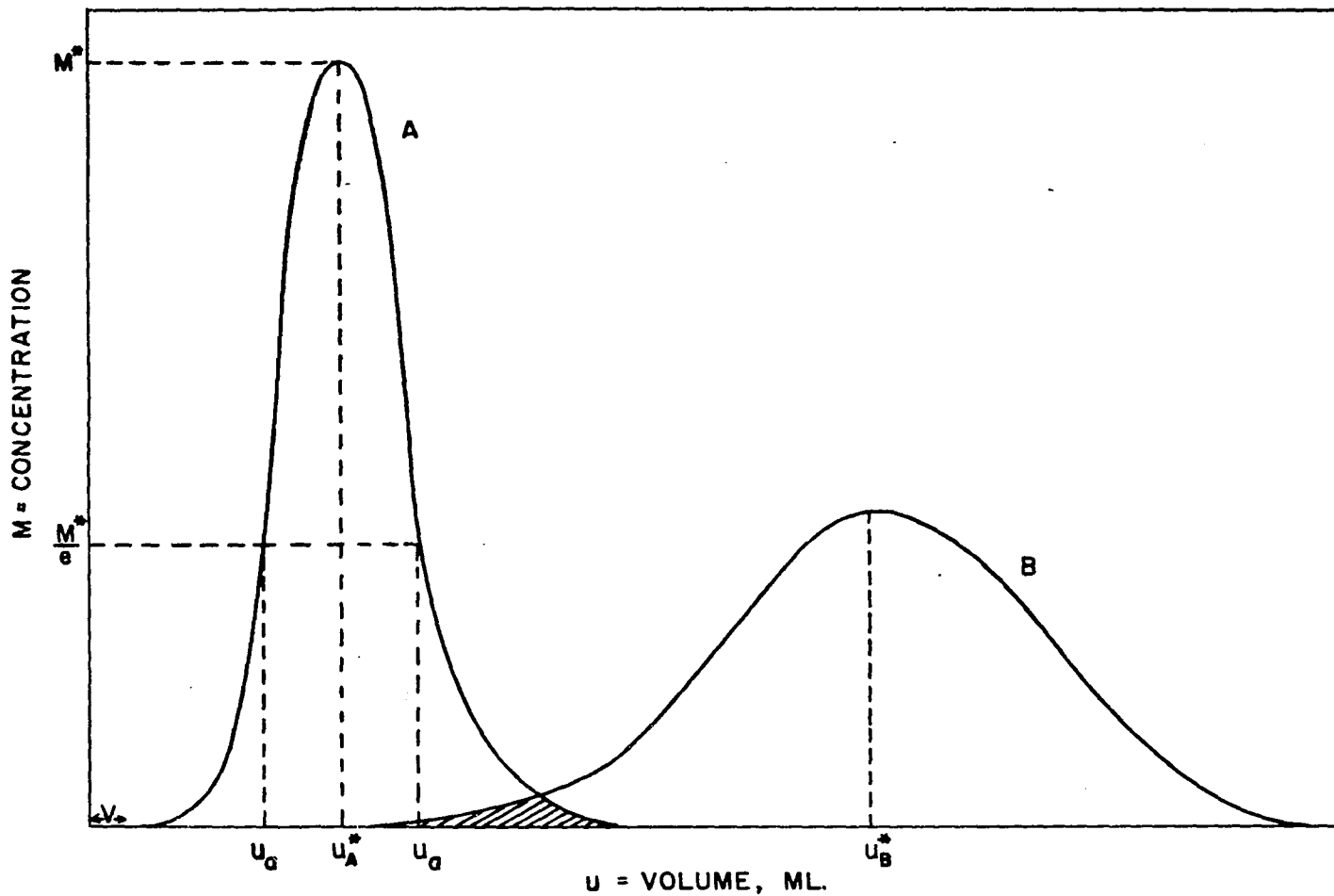


Figure 1. Typical elution curves for the separation of a divalent solute, A, and a trivalent solute, B.

$$k = \frac{D'_A}{D'_B} = \frac{U^*_A - V}{U^*_B - V} \quad (9)$$

This ratio, the selectivity coefficient, measures the tendency of the resin to separate the two solutes. It is the most important factor in elution chromatography, and can be determined from the single-element elution curves or by measuring the batch distribution coefficients for each solute. An increase in k gives rise to greater separations of the solutes. The nature of the eluant can exert considerable influence on D' and therefore on k . Equation 6 shows that D' varies inversely as the concentration of eluant raised to a power, z , equal to the charge on the ion being considered. If the ions differ in charge magnitude their respective distribution ratios will vary to different extents with a change in eluant concentration. The change being greater for the higher valent ions. If the charges are the same, no difference in k will be noticed with a change in eluant concentration. The effect of eluant pH must be considered when weak acids or weak bases are being separated because the amount of ionic species present in solution, and thus the distribution ratio, is dependent upon pH, the variation in D' being a function of the stability constants of the respective acid or base. When the solute forms a complex with the eluant, the distribution coefficients will be affected by the complexing ability of the reagent used as eluant. The separation coefficient will depend upon the stability constants

of the complexes formed (see page 37).

A practical approach to the separation of solutes affected by the nature of eluant would be to measure batch distribution coefficients of the individual components. A suitable eluant solution, one giving a good selectivity coefficient and low distribution coefficients, could be selected after a few measurements have been made. A major disadvantage to this approach is that the shapes of the elution curves cannot be predicted from batch measurements. The shape of the faster moving component, assuming near equilibrium conditions, will normally be narrow and symmetrical, but the curve for the slower moving component has a wide and often unsymmetrical shape. Even if the distribution data indicate that a large volume separates their respective peak maxima, the latter curve may overlap the former resulting in a poor separation. If fractions are being taken to collect each component, distribution data will not allow the breakthrough of the slower moving component to be predicted with any accuracy. In either case, single-element elution curves will complement the batch distribution data.

For separations where changes in concentration or pH of the eluant will not improve the separation, or the use of a complexing agent is useless or undesirable, the column height becomes important. From the single-element elution curves \underline{U}^* , \underline{M}^* , and \underline{M} are evaluated. Setting $\underline{U} = \underline{U}_a$ in equation 7, \underline{U}_a may be calculated. Substituting into equation 8 give \underline{p} , the number of theoretical plates. \underline{p} is not constant for any given column,

but changes with the ion being eluted and with the eluant. However, for any given column, solute, eluant, and flow rate p is constant. If all other conditions are fixed, p varies directly as the length of the column. Equation 10 can be used to calculate the minimum column height necessary to give a quantitative separation (99.9% complete) of two ions whose D' and P values are known. This equation is only an approximate form but it is sufficiently accurate for most purposes.

$$H = \frac{3.29}{(D'_B - D'_A)} \frac{D'_B + 0.5}{P_B} + \frac{D'_A + 0.5}{P_A} \quad (10)$$

The usefulness of these equations is based on the assumptions stated at the beginning of this section. For large mesh resins and fast flow rates, conditions of equilibrium are not attained and the results would be expected to deviate from those predicted. For heavily loaded columns, as in preparative work, deviations would also be expected.

Cornish (19) recently reviewed the application of the plate theory to analytical and preparative separations by ion-exchange elution. He also discussed the separation of lithium and sodium to give 99.999% pure products. His calculations showed that previous investigators "over-designed" their experiments. More complete and rigorous treatments of the plate theory may be found in previously mentioned references (4, 51, 52) and in the works of Glueckauf (33, p. 34, 34). Sen Sama et al. (65) found that for the separation of technetium and rhenium on

Dowex-1 elution with perchlorate ion that the trailing edges of the elution curves deviated markedly from those predicted by the plate theory. Explanations are given.

EXPERIMENTAL

Apparatus

A Beckman model-G pH meter equipped with a Beckman 1190-80 glass electrode and a Beckman 1170 calomel reference electrode, a Burrell shaker, a constant temperature device (Temp-unit: Arthur S. Lapine and Co.) and a Leeds and Northrup conductivity bridge were all the apparatus needed in this study. All volumetric glassware was class A.

Reagents

Ion-exchange resin: Dowex-50 X8 (50 - 100 mesh) hydrogen form. J. T. Baker Chemical Co. "analyzed reagent". The resin was converted to the ethylenediammonium form by exhaustive treatment with a solution of ethylenediammonium perchlorate.

Ethylenediamine: Eastman Kodax practical grade. Distilled prior to use.

Zinc metal: Primary standard zinc for melting point determination obtained from the National Bureau of Standards.

Rare earth oxides, uranium acetate, bismuth metal, and hafnium oxychloride (contains 2% zirconium): Ames Laboratory of the United States Atomic Energy Commission.

Aluminum metal: Alcoa Aluminum, spectrochemical standard SC1 - A high purity wire.

EDTA [disodium dihydrogen (ethylenedinitrilo) tetraacetate di-hydrate]: Sequestrene Na 2 recrystallized, as marketed by Geigy Industrial Chemical Co.

All other reagents were reagent grade laboratory chemicals.

Analytical Procedures

Standardization of ethylenediammonium solutions: Titrate conductometrically with a standard solution of sodium hydroxide.

Copper and Zinc: These metals were analyzed by the method of Fritz, Lane, and Bystroff (29).

Lanthanum and yttrium: These metals were analyzed by the method of Fritz, Oliver, and Pietrzyk (30).

Aluminum: Aluminum was analyzed by the back titration of excess EDTA with zinc (29).

Bismuth, zirconium, and hafnium: These metals were analyzed by the method of Fritz and Johnson (27). Zirconium and hafnium were also analyzed spectrophotometrically with alizarin red S according to the procedure of King and Owens (39).

Calcium, strontium, lead, and thorium: These metals were titrated with EDTA using methylthymol blue; calcium and strontium at pH 12 (1, p. 29), lead at pH 6 using pyridine as a buffer (1, p. 28), and thorium at pH 3 using an acetate buffer

(1, p. 29).

Barium: Barium was analyzed according to the procedure of Fritz and Yamamura (32).

Uranium: Uranium was analyzed by a modification of the method of Sill and Peterson (67). The uranium (IV) resulting from the reduction of uranium (VI) in a lead reductor was collected in an excess of ferric chloride and the ferrous iron determined as described in Diehl and Smith (24, p. 276).

Hydrogen ion: Hydrogen ion in the presence of ethylenediammonium ion, a weak acid, was determined by titration with standard base. The end point was determined conductometrically.

Measurement of Distribution Coefficients

The procedure for measuring distribution coefficients was as follows: One gram of air-dried resin was accurately weighed and placed in a 125 ml. ground-glass stoppered Erlenmeyer flask. To this was added a ml. of 1 M ethylenediammonium perchlorate (or the chloride salt) and (40 - a) ml. of water. Finally, 10 ml. of the metal solution containing 0.1 meq. of metal was added, and the flask stoppered and shaken for 12 hours or more at $25 \pm 0.5^{\circ}\text{C}$. Preliminary experiments showed that equilibrium was attained within an hour for all but the higher valent metal ions. After the samples had shaken, an aliquot of the solution phase was removed and analyzed. The

concentration of metal on the resin was found by difference. The distribution coefficient was calculated according to equation 11.

$$D = \frac{\text{meq. metal on resin/g dry resin}}{\text{meq. metal in solution/ml. of solution}} \quad (11)$$

The dry weight of the resin was calculated from the air dry weight and the moisture content of the resin.

To determine the moisture content of the resin a weighed amount of resin was dried at 100 - 110 °C for several hours and then placed in a vacuum desiccator under a vacuum for two or more hours. This procedure was found to give a minimum weight after two dryings. The moisture content was determined at the time the resin samples were weighed out, and varied from 19.9 percent during the initial experiments to 10.2 percent for the latter runs.

The procedure for measuring the distribution coefficients of lanthanum as a function of sodium salt concentration was the same as in the ethylenediammonium salt studies except that a ml. of 5 M sodium perchlorate or sodium chloride was used instead of the corresponding volume of 1 M ethylenediammonium solution.

Distribution coefficients for zinc, uranium (VI), yttrium, and thorium were measured as a function of temperature in 0.2 M ethylenediammonium perchlorate according to the procedure given at the beginning of this section. Flasks were equili-

brated in a constant temperature bath at 40°, 55°, 70°, and 81.5°C held to within $\pm 0.2^\circ\text{C}$.

The measurement of distribution coefficients for zinc, yttrium, lanthanum, and thorium as a function of initial metal ion concentration in 0.2 M ethylenediammonium perchlorate was carried out as described above. Distribution coefficients for copper and uranium were measured as a function of metal ion concentration also, but the solutions contained no initial ethylenediammonium ion. For all of these runs, the samples were prepared to contain 0.002 to 0.10 equivalents of metal ion per liter.

Column Behavior of Zinc and Yttrium

As a Function of Loading

Three single-element elutions were performed using 6.000g of air-dried resin in a 9 cm. by 12 mm. column. The columns were loaded with 0.1036, 0.5180, and 1.036 meq. of zinc respectively and 0.0999, 0.5995, and 0.999 meq. of yttrium respectively. Elutions were performed with 0.2 M ethylenediammonium perchlorate at pH 3, using a flow rate of approximately 10 ml. per 30 minutes. Fractions were collected in 10 ml. Rieman pipets and analyzed for metal content.

A column separation of a mixture containing 0.5180 meq. of zinc and 0.4995 meq. of yttrium was performed under conditions identical to those for the single-element elutions above.

RESULTS AND DISCUSSION

Distribution Coefficients as a Function of
Ethylenediammonium Ion Concentration

Distribution coefficients for uranyl perchlorate, copper perchlorate, zinc nitrate, calcium nitrate, strontium nitrate, barium chloride, lead perchlorate, and hydrogen ion measured in 0.0 to 0.2 M ethylenediammonium perchlorate solution are listed in Table 1. Those for lanthanum perchlorate, yttrium perchlorate, aluminum perchlorate, bismuth nitrate, thorium nitrate, zirconium perchlorate, and hafnium perchlorate measured in 0.0 to 1.0 M ethylenediammonium perchlorate solutions are listed in Table 2. Distribution coefficients for lanthanum perchlorate, yttrium perchlorate, aluminum perchlorate, thorium nitrate and zirconium perchlorate measured in 0.0 to 1.0 M ethylenediammonium chloride are given in Table 3. The distribution coefficients are plotted against the concentration of ethylenediammonium ion in Figures 2 and 3. As would be expected from Equations 13 and 14, D decreases with an increase in ethylenediammonium concentration and the decrease is greater for ions of higher charge. The selectivity coefficient for a given separation may be obtained by taking the ratio of the distribution coefficients obtained from these curves at a particular ethylenediammonium ion concentration.

The exchange of a metal cation for the ethylenediammonium

Table 1. Distribution coefficients for H⁺ and divalent metal ions in ethylenediammonium perchlorate solutions.

Metal	$\frac{[EnH_2^{+2}]}{M}$	0	0.002	0.01	0.02	0.04	0.05	0.06	0.08	0.1	0.2
H ⁺		10.5					9.6			6.0	4.9
		10.0					8.3			5.6	4.6
Cu ⁺²		84.1	69.0	41.3	27.6	16.5		12.8	10.4		
		80.3	66.4	40.5	27.8	16.9		12.5	10.0		
UO ₂ ⁺²		73.7	31.0	24.4	20.8	18.5		14.0	11.4		
Zn ⁺²		83.7					11.8			6.9	4.3
		83.7					11.9			8.0	4.3
Ca ⁺²		45.6					27.6			17.2	11.1
		46.1					27.2			17.0	11.2
Sr ⁺²		124					20.4			12.3	7.5
		124					20.4			12.1	7.5
Ba ⁺²		315					69.7			55.8 ^a	29.3
Pb ⁺²		308			101 ^b		64.7	49.5 ^c		41.1	26.4 ^d
		305			101		64.7	49.5		40.9	26.4

^aD = 38.1 at 0.015 M EnH₂⁺².

^bValues are for 0.025 M EnH₂⁺².

^cValues are for 0.075 M EnH₂⁺².

^dOther D values for Pb⁺²: 21.3, 21.3 at 0.3 M; 18.3 at 0.4 M; and 16.6 at 0.5 M EnH₂⁺².

Table 2. Distribution coefficients for tri- and tetravalent metal ions in ethylenediammonium perchlorate solutions.

Metal	$\left[\frac{\text{EnH}_2^{+2}}{\text{M}} \right]_0$	0.05	0.1	0.2	0.4	0.6	0.8	1.0
La ⁺³	3,022	169 ^a	119	59.0	33.5	26.0		24.5
	3,331	163	118	59.6	32.5	26.4		24.1
Y ⁺³	1,118		53.1	26.7	14.3	9.7		9.4
	1,118		53.1	27.2	14.3	9.7		9.1
Al ⁺³	1,138	178	133	108	96.7	95.6		93.9
	1,041	190	134	106	99.6	98.5		94.4
Bi ⁺³	1,752		880	687	561		561	
	1,881		968	742	561		561	
Th ⁺⁴	ca. 16,000			380	207	171	161	165
				384	207	168	159	166
Zr ⁺⁴ ^b							5,217	
							ca. 6,000	

^aValues are for 0.08 M EnH₂⁺²; Other values are 2,060 at 0.0025 M; 711,695 at 0.02 M; and 335 at 0.04 M EnH₂⁺².

^bZr⁺⁴ and Hf⁺⁴ were so strongly taken up by the resin that only estimated values could be obtained. D between 0 and 0.8 M EnH₂⁺² was estimated to be greater than 6,000.

Table 3. Distribution coefficients for tri- and tetravalent metal ions in ethylenediammonium chloride.

Metal	$\frac{[EnH_2^{+2}]}{M}$							
	0	0.1	0.2	0.4	0.6	0.8	1.0	
La ⁺³	3,022	83.0	34.4	13.6	7.2		4.7	
	3,331	83.8	33.9	13.4	7.3		4.9	
Y ⁺³	1,118	39.3	16.3	6.6	4.1		3.2	2.2
	1,118	39.3	16.3	6.6	4.1		2.7	2.0
Al ⁺³	1,138	124	101	92.7	89.6		88.6	
	1,041	127	103	93.7	86.9		86.0	
Th ⁺⁴	ca. 16,000			78.0	48.7		36.0	28.9
				78.1	48.3		37.6	29.8
Zr ⁺⁴	6,000	6,000	6,000	5,218		1,778		
				ca. 6,000		1,690		

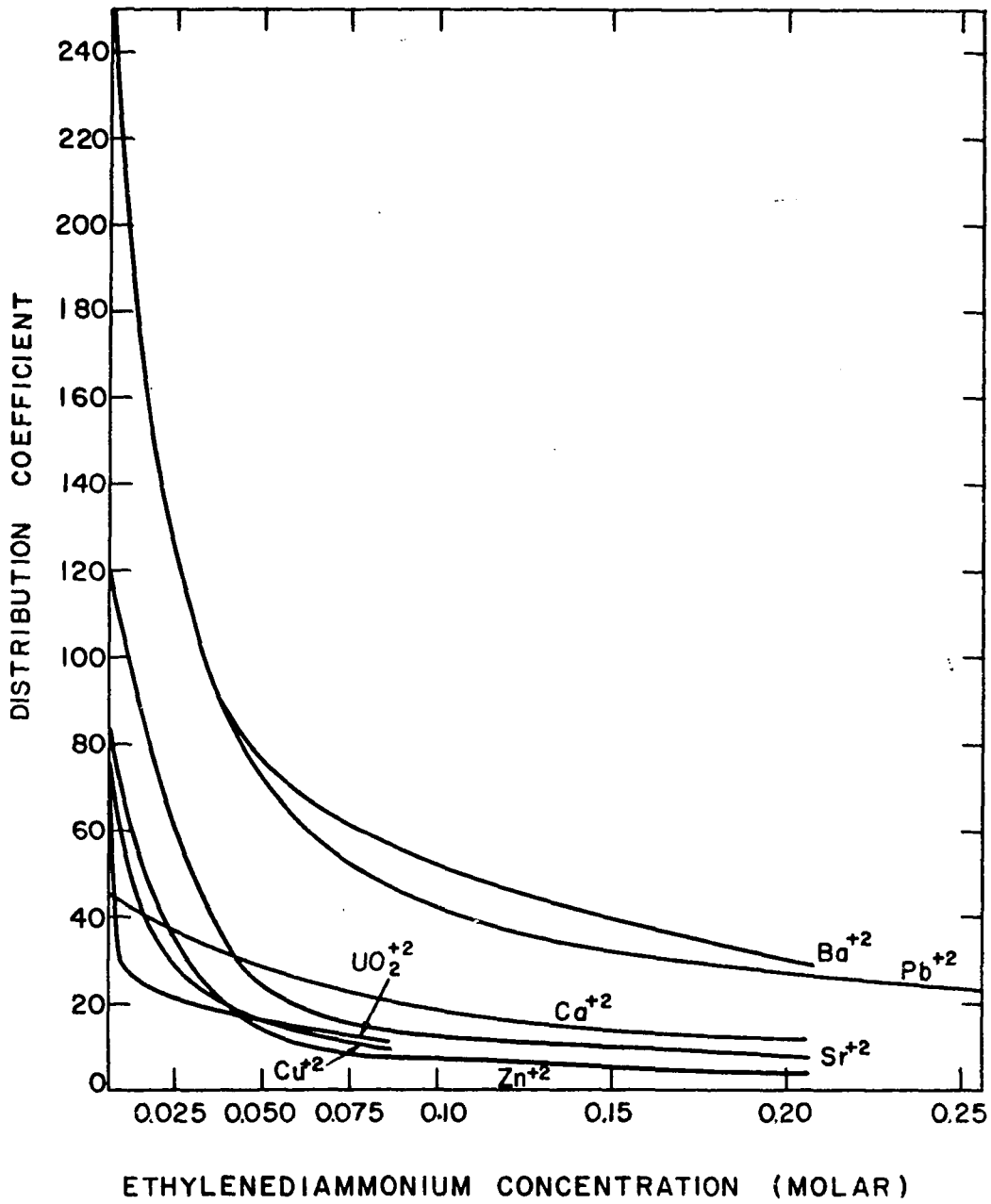


Figure 2. Equilibrium distribution of divalent metal ions vs. ethylenediammonium perchlorate concentration.

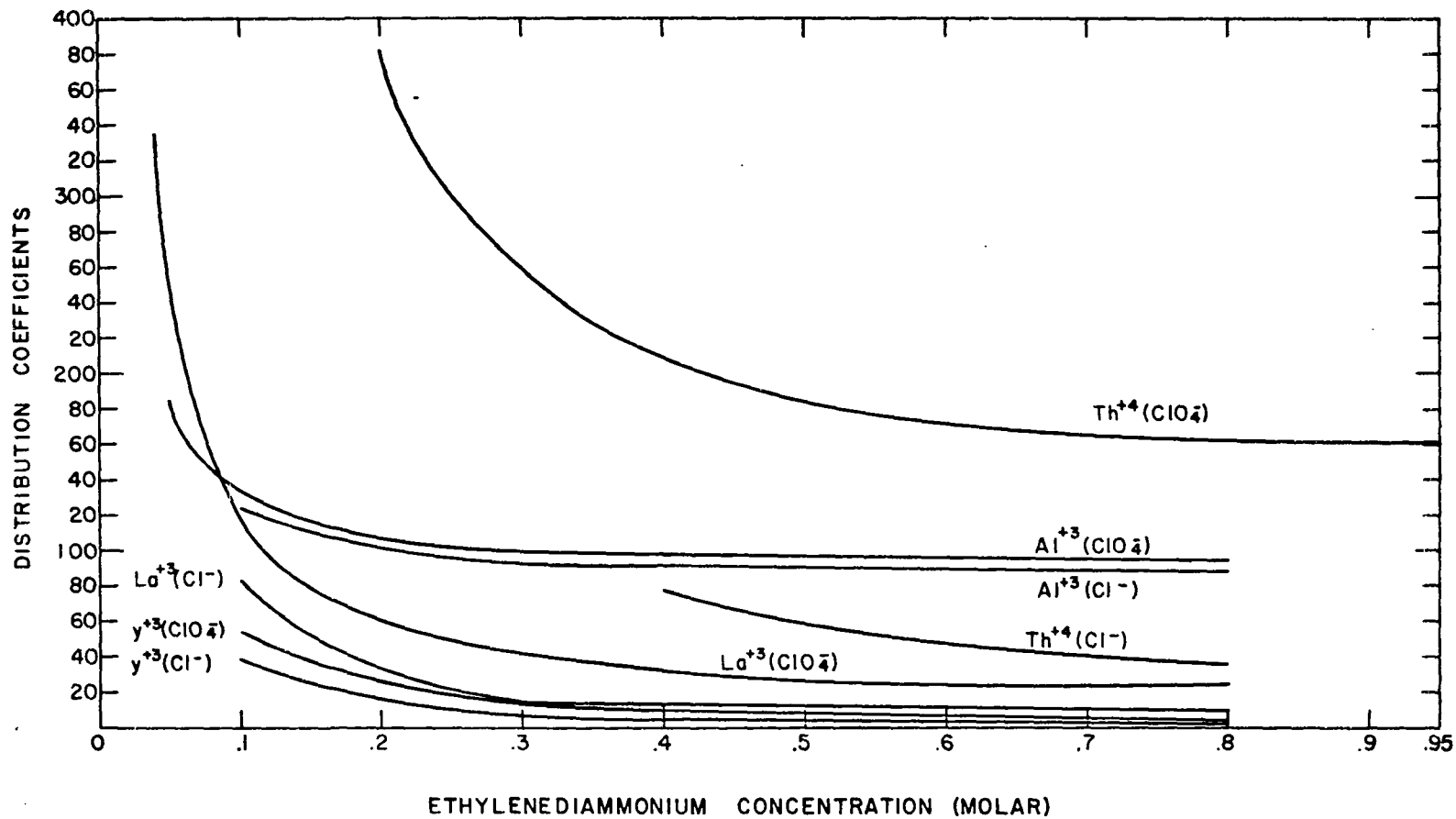
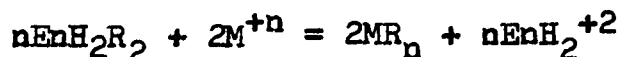


Figure 3. Equilibrium distribution of tri- and tetravalent metal ions vs. ethylenediammonium ion concentration.

form of a cation-exchange resin



may be treated according to the law of mass action to give an equilibrium constant, \underline{K} , expressed by the following equation

$$K = \frac{[\text{MR}_n]^2 [\text{EnH}_2^{+2}]^n}{[\text{M}^{+n}]^2 [\text{EnH}_2\text{R}_2]^n} \quad (12)$$

where the brackets, $[]$, represent concentrations. If at equilibrium, additional ethylenediammonium ion is added and equilibrium reestablished the concentration of the resin in the ethylenediammonium form may be assumed constant for low resin loadings. The assumption is more valid at higher ethylenediammonium concentrations. Equation 12 can be rearranged to give

$$K' = (\underline{D}')^2 [\text{EnH}_2^{+2}]^n \quad (13)$$

where \underline{D}' is the distribution ratio $[\text{MR}_n] / [\text{M}^{+n}]$ and is related to the distribution coefficient by

$$D = D' \frac{\text{no. ml. solution}}{\text{no. g resin}} \quad (14)$$

Taking the logarithm of Equation 13 gives

$$\log D' = \frac{\log K'}{2} - \frac{n}{2} \log [\text{EnH}_2^{+2}] \quad (15)$$

A plot of $\log \underline{D}'$ or $\log \underline{D}$ vs. $\log [\text{EnH}_2^{+2}]$ should give a straight line of negative slope $n/2$ if the assumption is valid. A straight line plot was obtained for all the metals

studied (Figures 4 and 5). The lines for lead, copper, calcium, strontium, barium, zinc, and uranium (VI) all have a negative slope of 0.5 between 0.02 and 0.2 M ethylenediammonium concentration. Yttrium and lanthanum give straight lines with a slope of -1 between 0.1 and 0.6 M ethylenediammonium solutions. The aluminum curve appears to have a slope of -1 between 0.01 and 0.05 M ethylenediammonium ion but the slope decreases at higher salt concentrations. Bismuth may behave like aluminum at lower ethylenediammonium concentrations, but gives a slope of -0.5 between 0.05 and 0.1 M ethylenediammonium perchlorate solutions. The thorium curve has a slope of -1 in the same concentration range as for bismuth for both the perchlorate and chloride salts. It may, however, have a higher slope at lower ethylenediammonium concentrations.

For the divalent and trivalent ions, except bismuth, the slope of the line is $-(n - 1)/2$ instead of $-n/2$. This suggests that the ion being adsorbed has a charge one less than that expected. For thorium and bismuth the slope is $-(n - 2)/2$. Hydrolysis, electrostatic effects within the resin, or polymerization (36, 37) may be contributing factors to this unexpected lowering of the slope.

Effect of Chloride Ion on the Distribution Coefficients

Figures 5 and 6 show a pronounced lowering of the distribution coefficients when ethylenediammonium chloride is used in place of the perchlorate salt. This lowering is easily explain-

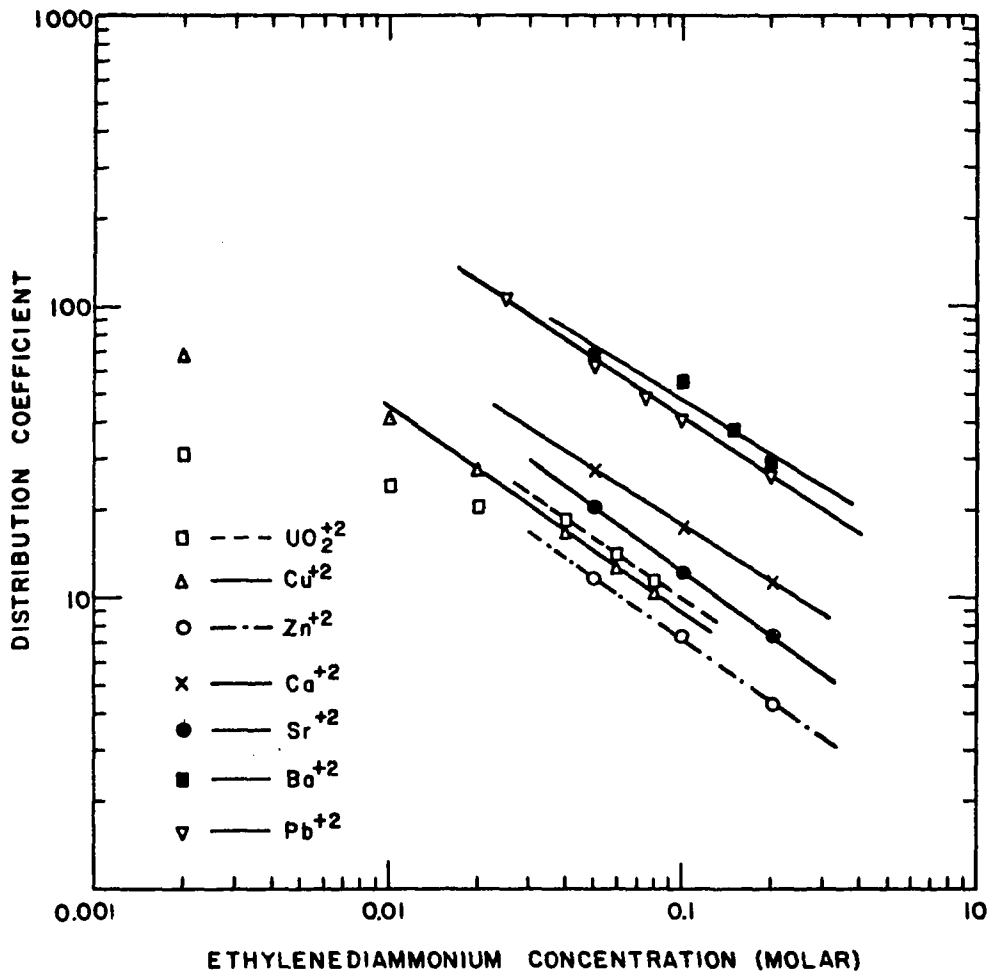


Figure 4. Equilibrium distribution of divalent metal ions vs. ethylenediammonium perchlorate concentration. A plot of Equation 15.

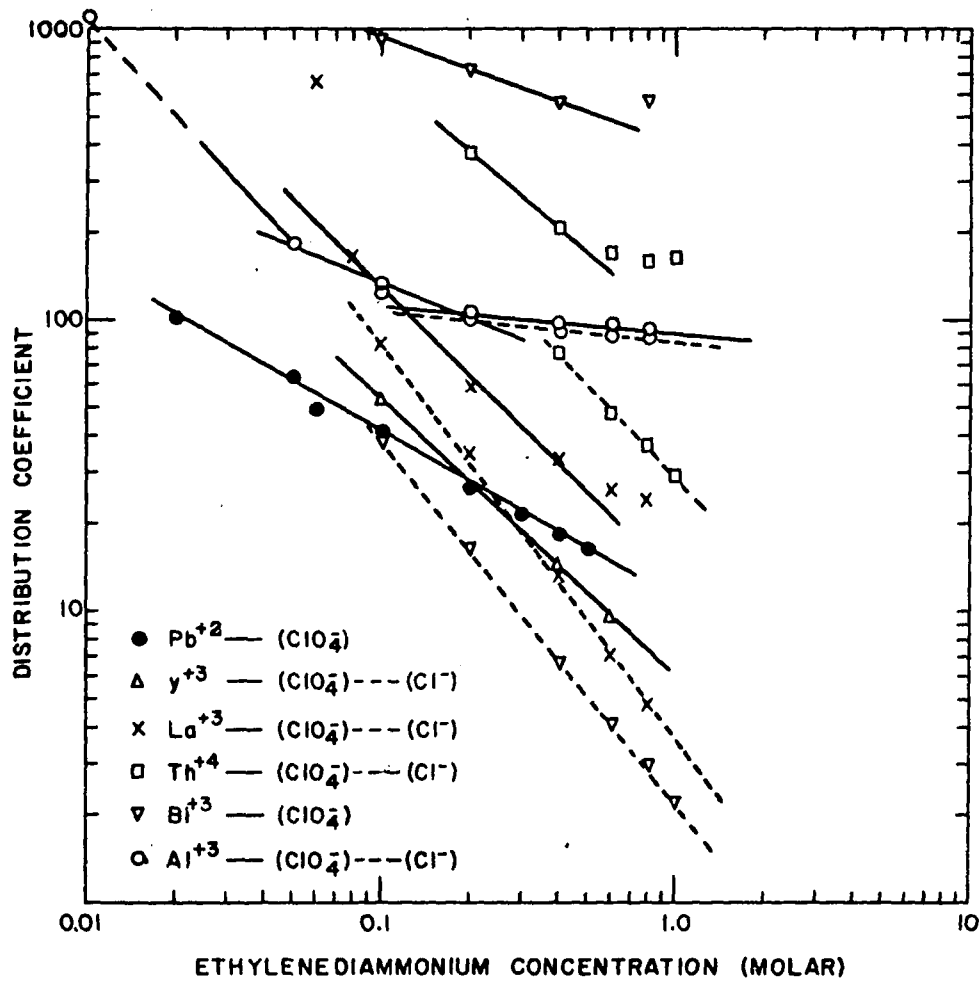


Figure 5. Equilibrium distribution of tri- and tetravalent metal ions vs. ethylenediammonium perchlorate and ethylenediammonium chloride concentration. A plot of Equation 15.

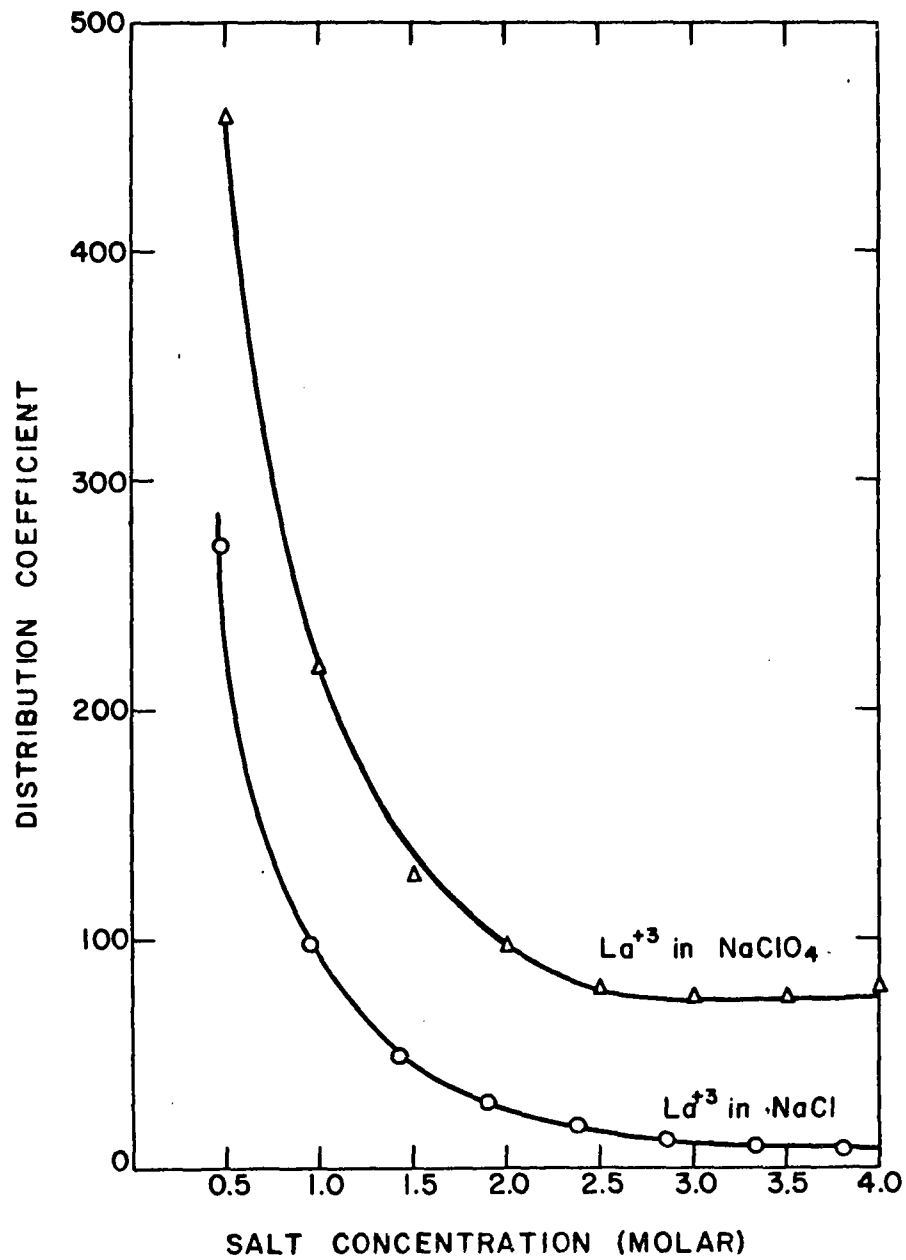


Figure 6. Equilibrium distribution of La^{+3} vs. sodium salt concentration.

ed on the bases of chloride complexing. In the presence of a complexing agent an expression analogous to Equation 14 is used to express the distribution coefficient of the metal, D_o :

$$D_o = \frac{[MR_n]}{[M^{+n}] + [MX_m^{+n-m}]} \quad (16)$$

where X^{-1} represents halide ion. It is assumed that only one complex is being formed. From the stability constant expression for the complex

$$K_1 = \frac{[MX_m^{+n-m}]}{[M^{+n}][X^{-1}]^m}$$

the concentration of MX_m^{+n-m} can be evaluated in terms of K_1 , M^{+n} , and X^{-1} . Substituting Equations 11 and 17 into 16

$$D_o = \frac{[M^{+n}] D}{[M^{+n}] + K_1 [M^{+n}][X^{-1}]^m} \quad (18)$$

or

$$D_o = \frac{D}{1 + K_1 [X^{-1}]^m} \quad (19)$$

Rearrangement gives

$$\frac{D}{D_o} - 1 = K_1 [X^{-1}]^m \quad (20)$$

or

$$\log \left(\frac{D}{D_o} - 1 \right) = \log K_1 + m \log [X^{-1}] \quad (21)$$

A plot of $\log (D/D_o - 1)$ vs. $\log [X^{-1}]$ should give a straight

line with slope \underline{m} , the number of complexing species per complex, and intercept \underline{K}_1 , the stability constant of the complex formed.

The data for lanthanum, yttrium, and thorium (see Table 4) are plotted according to Equation 21 as shown in Figure 7. The yttrium curve has a slope of 0.9 while the thorium slope is 1.0. In both systems a 1:1 chloride-metal complex is formed. The lanthanum curve has two slopes, one 0.85, the other 1.7. This implies a 1:1 and possibly a 2:1 complex being formed.

Table 4. Variation of distribution coefficients with chloride concentration.

	$\left[\frac{\text{EnH}_2^{+2}}{\underline{M}} \right]$	$\left[\frac{\text{Cl}^-}{\underline{M}} \right]$	D	D ₀	$\frac{D}{D_0} - 1$
La ⁺³	0.10	0.20	118	83.4	0.42
	0.20	0.40	59.3	34.1	0.74
	0.40	0.80	33.0	13.5	1.44
	0.60	1.20	26.2	7.3	2.61
	0.80	1.60	24.3	4.8	4.06
Al ⁺³	0.10	0.20	133	125	0.06
	0.20	0.40	107	102	0.05
	0.40	0.80	98.2	93.2	0.05
	0.60	1.20	97.1	88.3	0.10
	0.80	1.60	94.2	87.3	0.08
Y ⁺³	0.10	0.20	53.1	39.3	0.35
	0.20	0.40	26.9	16.3	0.65
	0.40	0.80	14.3	6.63	1.16
	0.60	1.20	9.7	4.1	1.35
	0.80	1.60	9.2	2.9	2.17
Th ⁺⁴	0.10	0.20			
	0.20	0.40			
	0.40	0.80	207	78.0	1.65
	0.60	1.20	170	48.5	2.51
	0.80	1.60	160	36.8	3.35
	1.00	165	29.4	4.61	

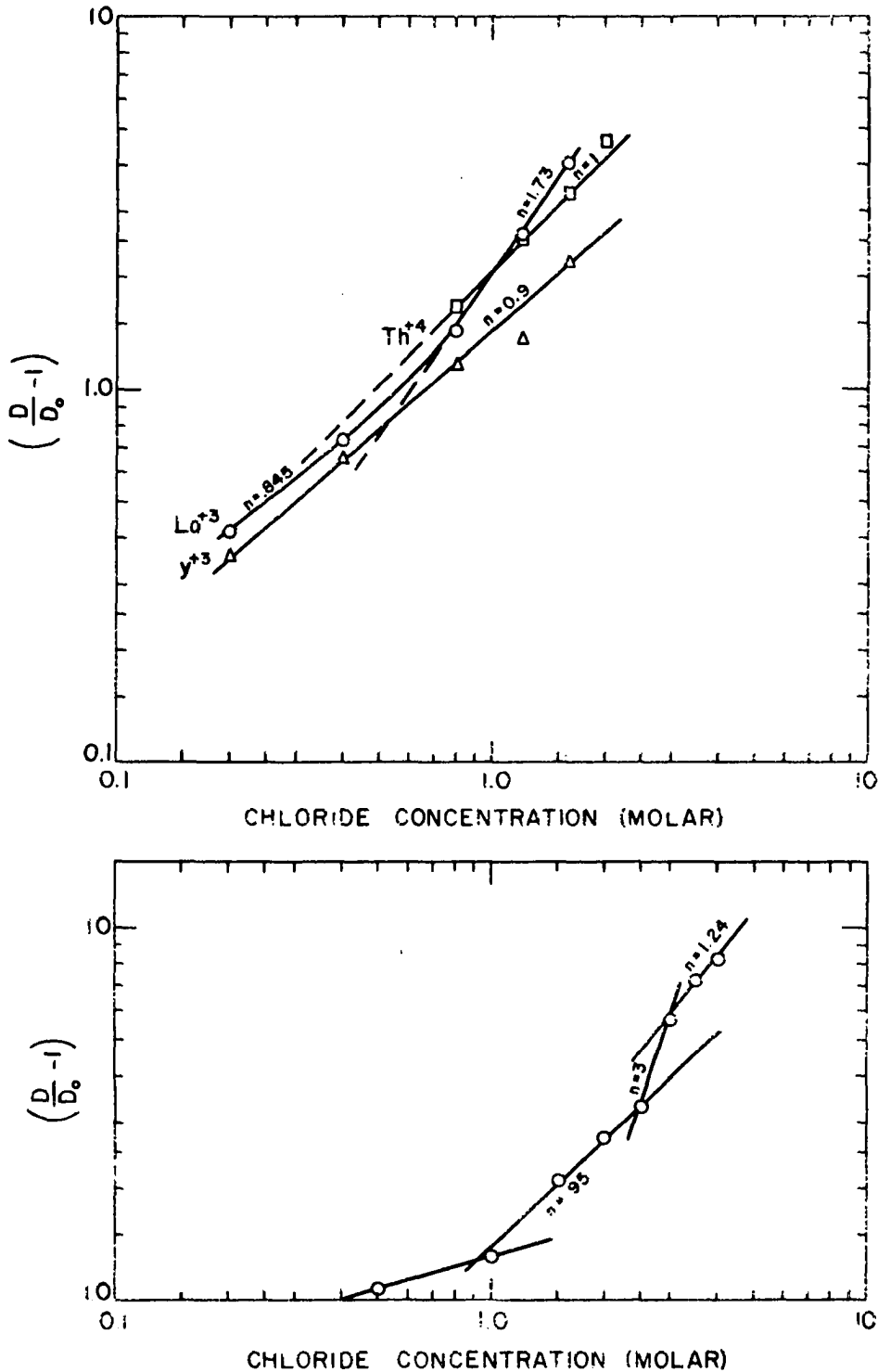


Figure 7. Determination of chloride complex formation by ion-exchange adsorption. Top: In ethylenediammonium salt solutions. Bottom: For La^{+3} in sodium salt solutions.

Data for the lanthanum distribution coefficients measured in the sodium salt systems (see Table 5) are plotted in Figures 6 and 7. An m of 0.95 in Figure 7 shows the existence of a 1:1 chloro complex is formed between 1.0 and 2.5 M chloride ion. Between 2.5 and 3.0 M chloride ion a slope of 3 is observed showing that a higher complex is formed; possibly a 3:1 neutral species. Above 3 M chloride concentration the curve slopes off, probably owing to no further complexing of the lanthanum. Aluminum exhibits a decrease in distribution coefficient in the presence of chloride ion but the data (see Table 4) does not show evidence of a chloride complex. The observed difference in distribution coefficients may be due to a difference in activities of the adsorbable species in the two solutions.

Equilibrium constants for the 1:1 complexes of yttrium, lanthanum, and thorium, taken from Figure 7, were found to be 1.44, 1.65, and 2.08 respectively for the ethylenediammonium salt studies and 1.40 for lanthanum using sodium salts. The equilibrium constants for lanthanum and thorium agree quite well with literature values of 0.68 to 0.78 for lanthanum (18) and 1.78 for thorium (71).

The complexing effect of the anion associated with the eluant ion is quite significant in column separations. The distribution coefficients for thorium and zirconium in ethylenediammonium perchlorate are very high (see Table 2). This means that the elution of these ions with the above eluant

Table 5. Variation of distribution coefficients for La^{+3} in 0.5 to 4.0 M NaClO_4 and NaCl solutions.

$\left[\frac{\text{NaClO}_4}{\text{M}} \right]$	$\left[\frac{\text{NaCl}}{\text{M}} \right]$	D	$D(\text{corr.})^a$	D_0	$D_0(\text{corr.})^a$	$\frac{D}{D_0} - 1^a$
0.5	0.475	457	457	272	220	1.08
1.0	0.95	218	218	98.5	94	1.32
1.5	1.425	128	140	49.8	45	2.11
2.0	1.90	96.6	98	29.5	26	2.77
2.5	2.375	78.4	78	19.6	18	3.33
3.0	2.85	74.2	74	12.9	11	5.73
3.5	3.325	74.1	74	10.5	9	7.22
4.0	3.80	78.4	74	8.7	8	8.25

^aValues corrected graphically - see Figure 7.

would be difficult and a separation impractical or even impossible. However, by changing the eluant to the chloride salt and increasing its concentration to 2 M it may be possible to lower the distribution coefficients sufficiently, owing in part to the formation of chloride complexes, to effect a separation in a reasonable length of time. In the separation of rare earths from thorium, the rare earth may be eluted with ethylenediammonium perchlorate leaving the thorium behind. For reasons just mentioned, the thorium band will move very slowly under these conditions and also become diffuse. By changing to the chloride salt the thorium band will travel faster and be removed from the column in a smaller volume.

Most anions form complexes. By the appropriate choice of the anion associated with the eluant separations may be made quicker and easier. Very weak complexes may be detected and their stability constants measured by comparing ion-exchange distribution coefficients in eluant solutions containing a non-complexing anion with those measured in solutions containing a complexing anion.

Effect of Temperature on the Distribution Coefficients

The distribution coefficients of zinc, uranium (VI), yttrium, and thorium were measured at 40°, 55°, 70°, and 81.5°C. The data are tabulated in Table 6. Figure 8 shows that the logarithm of the distribution coefficient varies linearly with $1/T$ (T is the absolute temperature). This would be expected if

Table 6. Distribution coefficients of metal ions in 0.2 M $\text{EnH}_2(\text{ClO}_4)_2$ as a function of temperature between 2.5 °C and 81.5 °C.

Metal	T°C	25	40	55	70	81.5
UO_2^{+2}			9.4	11.6	15.0	17.1
			9.4	12.2	14.9	17.2
Zn^{+2}		4.3	4.4	4.7	5.0	5.1
		4.3	4.4	4.5	5.3	5.0
Y^{+3}		27.0	31.5	39.2	49.7	60.0
			31.2	39.5	49.4	59.4
Th^{+4}		370	1,185	2,264	5,519	11,260
			1,125	2,108	5,940	10,680

the heats of reaction, ΔH , for the ion-exchange equilibria were constant and independent of temperature. Strictly speaking, it is the logarithm of the equilibrium constant which would vary linearly with $1/T$ but \underline{D} and \underline{K} are proportional at substantially constant resin and solution compositions as is the case here (see Table 7). Kraus and Raridon (44, 45) studied the adsorption of trace-metal ions on the hydrogen form of Dowex-50 from perchloric acid or sodium salt (NaClO_4 or NaCl) solutions. The logarithm of the distribution coefficient did not vary linearly with $1/T$ but fitted the function

$$\log D = A' \log T + B'/T + C' \quad (22)$$

which holds when the difference in heat capacities of the products and reactants are constant.

If Equation 12 is rewritten in the form

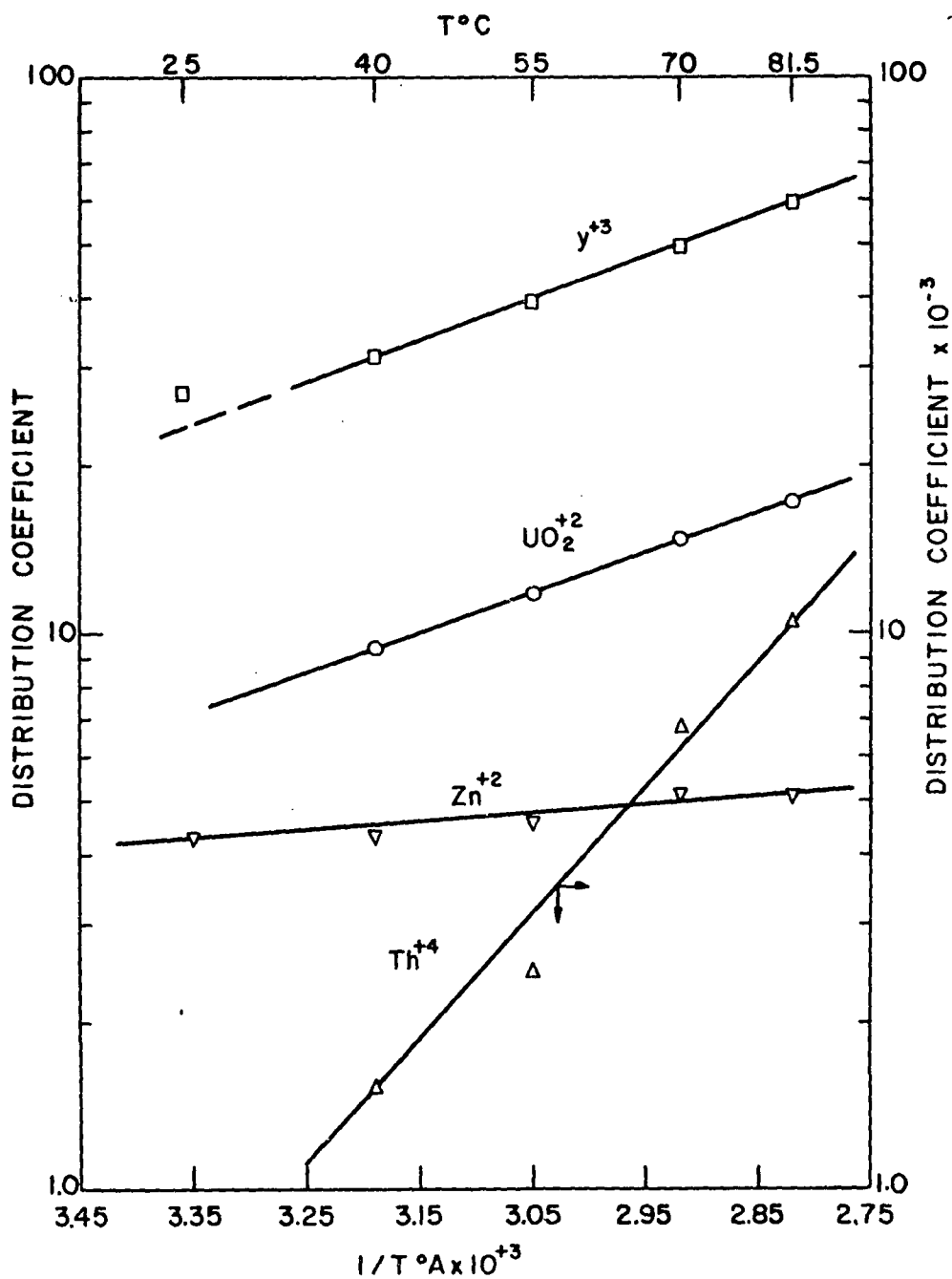


Figure 8. Temperature dependence of distribution coefficients. (Arrows refer to coordinates.)

Table 7. Ion-exchange equilibria as a function of temperature.

Each sample contained 1.000g EnH_2^{+2} resin (=4.69 meq.)
 10 ml 0.10 N metal ion in a total vol. of 50 ml. 0.2
M in ethylenediammonium perchlorate.

Metal	T °C	X	Y_{metal} Eq./l $\times 10^2$	$Y_{\text{EnH}_2^{+2}}$ Eq./l $\times 10^2$	K
UO_2^{+2}	40°	0.0846	4.69	4.08	0.81
		0.0852	4.68	4.08	0.81
	55°	0.101	4.53	4.10	1.02
		0.105	4.49	4.10	1.07
	70°	0.125	4.31	4.12	1.36
		0.124	4.32	4.12	1.35
	81.5°	0.138	4.19	4.13	1.58
		0.139	4.18	4.13	1.59
Zn^{+2}	40°	0.0163	1.92	4.02	0.35
		0.0162	1.92	4.02	0.35
	55°	0.0173	1.91	4.02	0.37
		0.0166	1.92	4.02	0.35
	70°	0.0184	1.90	4.02	0.40
		0.0194	1.89	4.02	0.42
	81.5°	0.0187	1.90	4.02	0.40
		0.0184	1.90	4.02	0.40
Y^{+3}	40°	0.0514	0.847	4.05	2.86 $\times 10^3$
		0.0511	0.850	4.05	2.80
	55°	0.0591	0.778	4.06	4.62
		0.0591	0.775	4.06	4.66
	70°	0.0671	0.700	4.06	7.58
		0.0669	0.702	4.06	7.52
	81.5°	0.0737	0.638	4.07	11.33
		0.0734	0.641	4.07	11.10

Table 7 (Continued).

Metal	T °C	X	Y_{metal} Eq./l $\times 10^2$	$Y_{\text{EnH}_2^{+2}}$ Eq./l $\times 10^2$	K
Th ⁺⁴	40°	0.101	3.32	4.10	6.33
		0.102	3.52	4.10	6.06
	55°	0.103	2.36	4.10	9.11
		0.103	2.00	4.10	10.83
	70°	0.104	0.80	4.10	27.3
		0.104	0.80	4.10	27.3
	81.5°	0.104	0.52	4.10	42.0
		0.105	0.52	4.10	42.3

$$K = \frac{x^2(y_{\text{EnH}_2^{+2}})^n}{(1-x)^n(y_{\text{M}^{+n}})^2} \quad (23)$$

where \underline{x} is the mole fraction of the metal resin at equilibrium and \underline{y} is the equivalent fraction of the designated ion in solution, equilibrium constants and be calculated from the experimental data. Values of \underline{K} are tabulated in Table 7. The variation of $\log \underline{K}$ with $1/T$ is linear as predicted (see Figure 9). The heat of reaction may be calculated from the slope of the curve according to the van't Hoff equation

$$\log K = \frac{-2.303 \Delta H}{RT} + C \quad (24)$$

or, with ΔH in calories, so that \underline{R} is 1.987

$$\log K = \frac{-\Delta H}{4.576T} + C \quad (25)$$

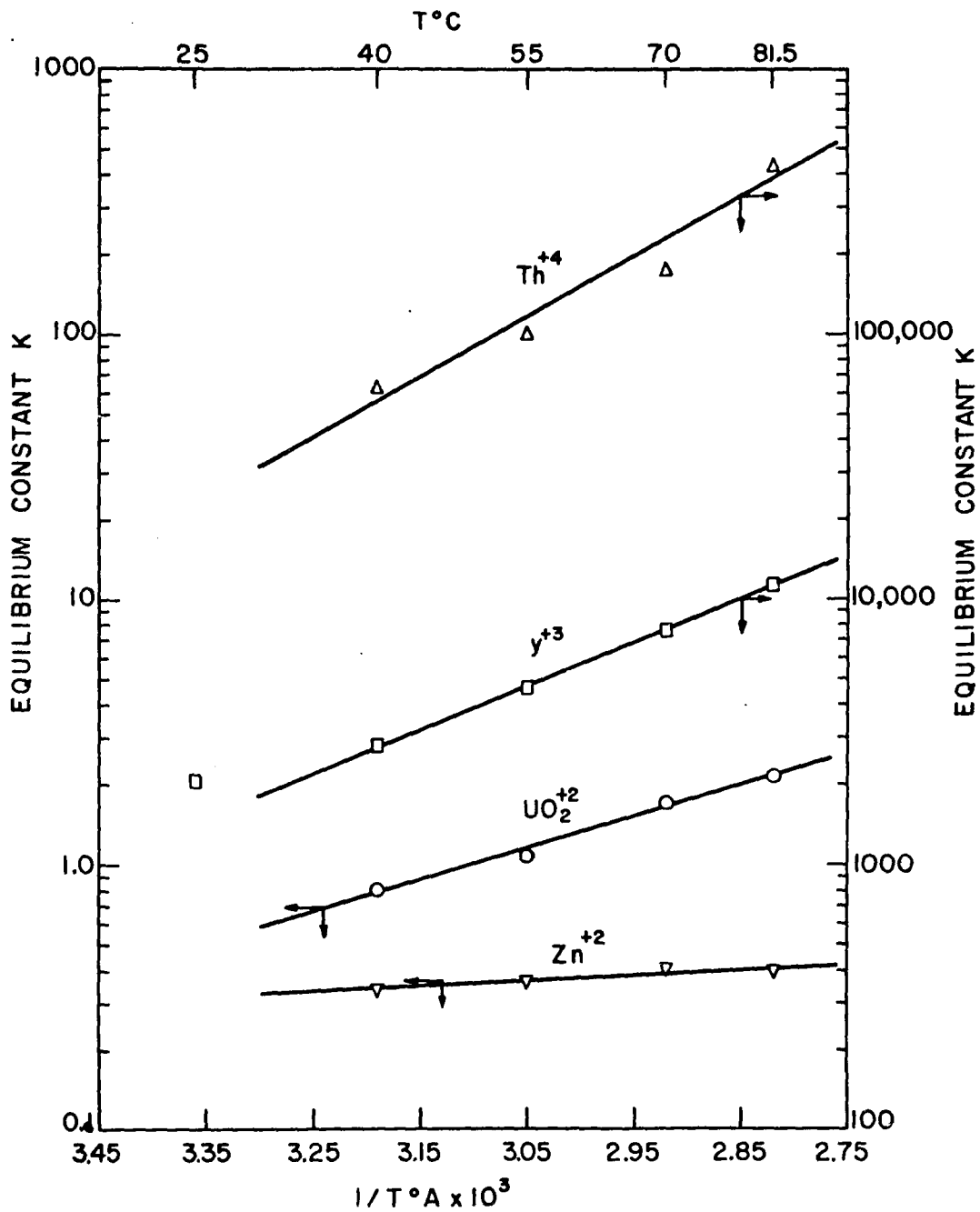


Figure 9. Temperature dependence of the exchange equilibrium constant. (Arrows refer to coordinates.)

The values of ΔH calculated from Figure 9 are shown in Table 8. These values are of the same order of magnitude as other values found in the literature (11, 44). Bonner and Smith (11) found that the $\log K$ vs. $1/T$ plots for the cupric-hydrogen and sodium-hydrogen exchanges followed a straight line between 0° and 75°C but deviated slightly at higher temperatures. The resultant values of ΔH were negative, indicating an exothermic process, for the sodium-hydrogen exchange and positive, i.e., endothermic, for the cupric-hydrogen exchange. Their observations are in agreement with those of Kraus and Raridon (44).

Table 8. Apparent enthalpy changes for cation-exchange equilibria.

Ion	$\frac{-\Delta H}{4.576}$	ΔH (kcal)
Zn ⁺²	-0.083	0.018
UO ₂ ⁺²	-0.396	0.087
Y ⁺³	-0.806	0.176
Th ⁺⁴	-0.681	0.149

Figures 8 and 9 clearly indicate the practical importance of temperature in column separations. For example, distribution data predicts that uranium (VI) would be eluted slower at high temperature while zinc would show no appreciable change. This has been shown experimentally.¹ The selectivity coefficient

¹Karraker, S. K. "Ion-exchange separations based on ion charge," Private communication, Ames, Iowa (1959).

for the uranium (VI)-zinc separation is 1.6 at 25°C and 3.4 at 81.5°C; an increase of over 200%. The slopes of the yttrium and uranium (VI) curves are nearly the same, and there is only a 1.6% increase in the selectivity coefficient for these ions over the temperature range studied. The thorium curve rises much more rapidly than any of the others and can probably be separated from any di- or trivalent ion at 81.5°C.

Effect of Initial Metal Concentration
on the Distribution Coefficients

To complete this study, it was of interest to see how the distribution coefficient varied with initial metal ion concentration and to compare it with column behavior. The distribution data for zinc, yttrium, lanthanum, and thorium in 0.2 M ethylenediammonium perchlorate solutions is given in Table 9 and for copper and uranium (VI) with no ethylenediammonium ion

Table 9. Distribution coefficients of metal ions in 0.2 M $\text{EnH}_2(\text{ClO}_4)_2$ as a function of initial metal ion concentration.

Metal $\left[\frac{\text{Metal}}{\text{Eq./l}} \right]$	0.002	0.01	0.02	0.04	0.08
Zn ⁺⁴	5.5	4.3	4.3	4.5	4.12
Y ⁺³	30.5	28.1	27.0	21.4	17.2
La ⁺³	73.3	64.5	62.0	45.6	31.7
Th ⁺⁴	1,162	1,469	370	348	106

present in Table 10. Log-log plots of these data are shown in Figures 10 and 11 respectively.

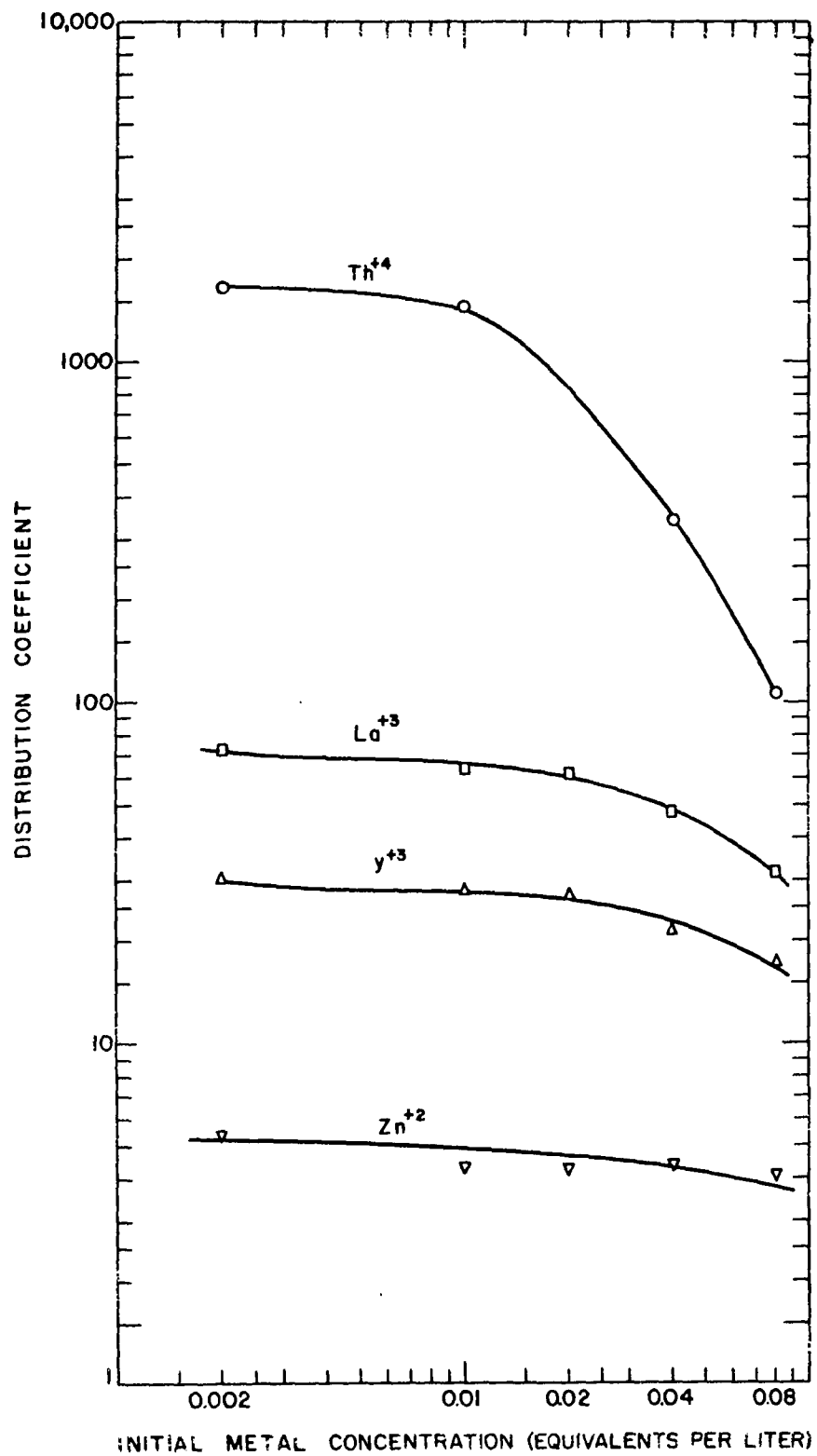
When the distribution coefficients are low, as for zinc, $\log D$ remains almost constant over the concentration range studied. However, for thorium where the distribution coefficient is much higher, $\log D$ decreases slowly at first then drops off rapidly with increasing metal concentrations. Yt-

Table 10. Distribution coefficients of Cu^{+2} and UO_2^{+2} as a function of initial metal ion concentration.

Metal	[Metal] Eq./l	0.002	0.01	0.02	0.04	0.06	0.08	0.10
Cu^{+2}		591	149	80.8	45.7	33.4	26.9	22.2
		591	149		45.7	33.4	28.7	22.8
UO_2^{+2}		292	70.8	37.9	21.1	14.9	12.0	10.3
			70.8	38.3	21.3	15.4	12.1	10.1

trium and lanthanum show behavior in between that of zinc and thorium. These batch experiments suggest that since the distribution coefficient of a metal ion decreases with increasing metal concentration, the metal should be eluted more rapidly from a column of resin with increased loadings. This was actually observed when zinc and yttrium were eluted from a 9 cm. x 12 mm. column containing 6 g of air-dried resin in the ethylenediammonium form. The columns were loaded with 0.1, 0.5, and 1.0 meq. of zinc or yttrium and eluted with 0.2 M ethylenediammonium perchlorate at pH 3. Figure 12 shows the

Figure 10. The effect of initial metal ion concentration on the distribution coefficient in 0.2 M ethylenediammonium perchlorate solutions.



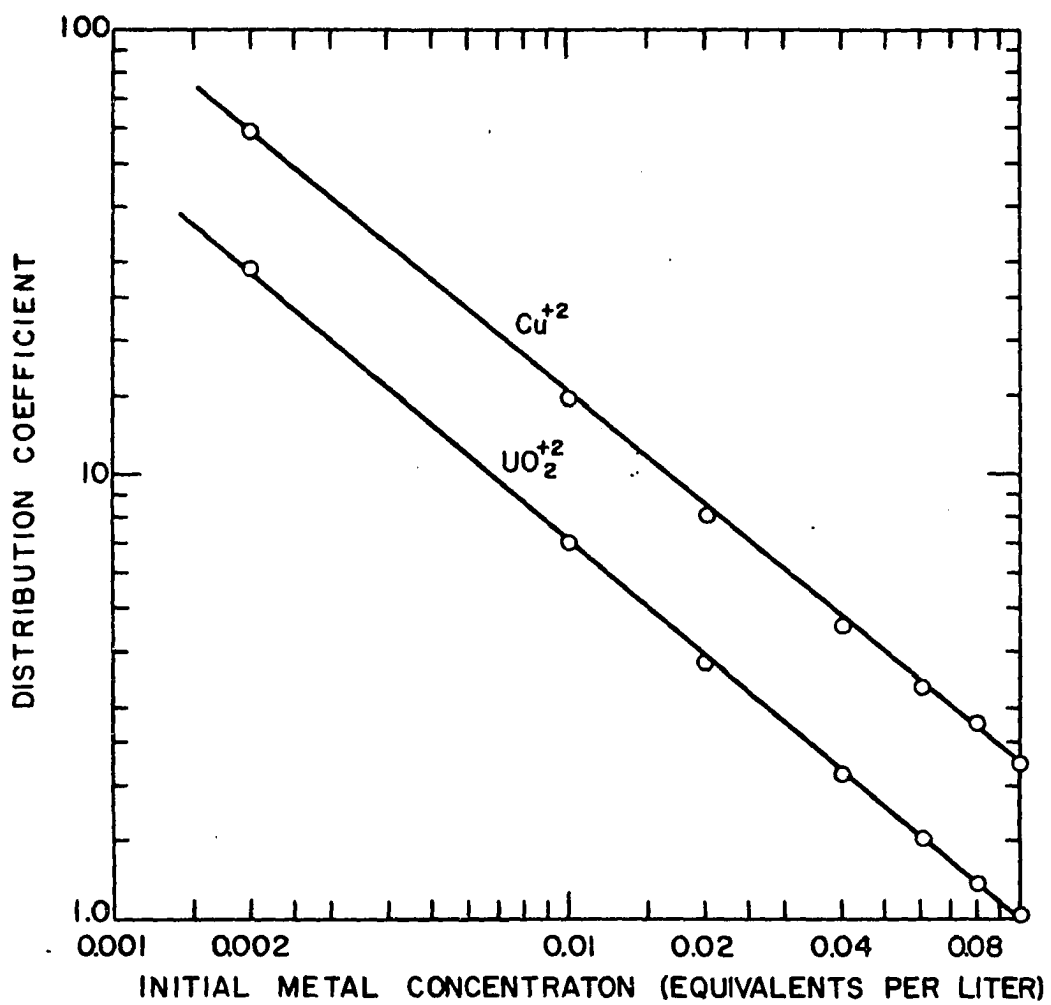


Figure 11. The effect of initial metal ion concentration on the distribution coefficient without added ethylenediammonium ion.

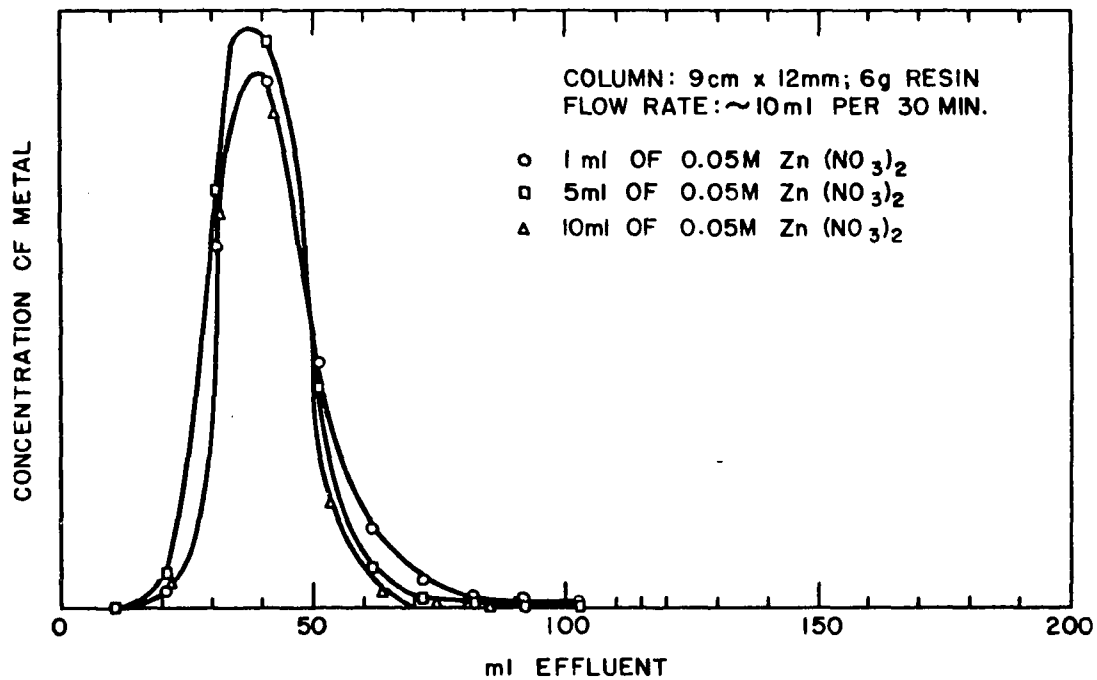
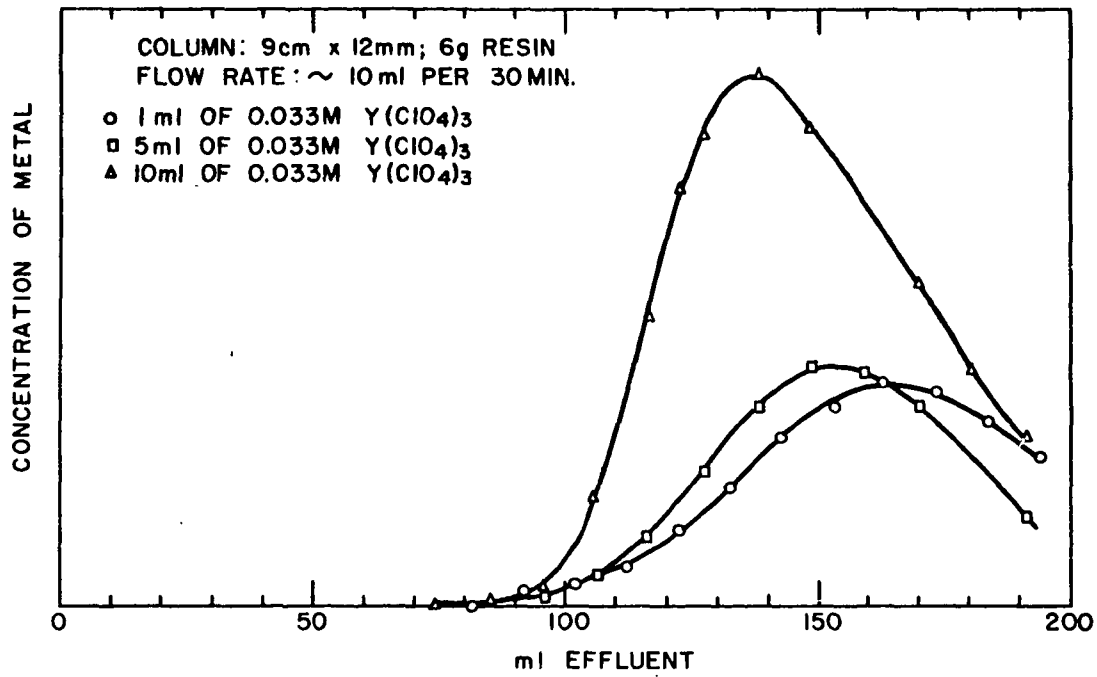


Figure 12. Single-element elution curves as a function of column loading; 0.2 M ethylenediammonium perchlorate, pH 3, eluant. Top: Y^{+3} . Bottom: Zn^{+2} .

single-element elution curves for these runs. The change in the elution peaks is not quite as obvious for the zinc curves as it is for the yttrium curves. However, the latter clearly shows that the elution peaks are shifted toward smaller volumes at higher loadings. This confirmed that a lowering of the distribution coefficients is brought about by an increase in the amount of metal ion present. From these results it would appear that the limits of any binary separation, based on charge magnitude, would depend upon the maximum concentration of the higher charged species and the minimum concentration of the lower charged species.

The behavior of the distribution coefficient with increasing concentration of metal ion in the absence of ethylenediammonium ion is quite different from that above. The $\log D$ vs. $\log [\text{metal}]$ plots for copper and uranium (VI) give straight lines (Figure 11) of rather steep negative slope. The rapid decrease of $\log D$ with the increased metal concentration at low metal concentration is believed to be due to the rapid change in the ionic strength of the solution with the addition of metal salt. In 0.2 M ethylenediammonium perchlorate solutions the ionic strength does not change as drastically when the metal salt concentration is increased. This difference in behavior means that when 0.2 M ethylenediammonium perchlorate (or higher concentrations) is used as eluant that separations are not extremely dependent on metal concentration. The elution behavior of the higher valent ions, es-

pecially for thorium, is more sensitive to metal ion concentration than the others. This was shown experimentally in the separation of rare earths from thorium.¹ During a chromatographic elution of equal molar concentrations rare earths and thorium from a 6 cm. by 12 mm. column with 0.5 M ethylenediammonium perchlorate the thorium band overlapped that of the rare earths. By decreasing the concentration of thorium to one-half the original amount, placing the distribution coefficient nearer to the straight line portion on the thorium curve (see Figure 10), a complete separation was obtained.

¹Karraker, ibid.

SUMMARY

1. The batch distribution coefficients of fifteen common metal cations were measured as a function of ethylenediammonium perchlorate concentration using Dowex-50 X 8 (50-100 mesh) in the ethylenediammonium form. From a plot of the distribution coefficients vs. ethylenediammonium concentration for each metal studied, the strength of eluant necessary to effect a quantitative separation may be obtained.

2. The distribution coefficients for yttrium, lanthanum, aluminum, and thorium were found to be lower in ethylenediammonium chloride solutions than in the corresponding concentrations of ethylenediammonium perchlorate. A 1:1 chloride-metal complex was formed with yttrium, lanthanum, and thorium. Stability constants were calculated from these data.

3. The variation of distribution coefficients for a di-, a tri-, and a tetravalent ion was studied as a function of temperature between 25° and 81.5°C. Heats of reaction were calculated from the data according to the van't Hoff equation.

4. The effect of initial metal ion concentration of the distribution coefficients of metal ions was studied by both batch and column experiments.

5. The separation of zinc and yttrium was accomplished by using conditions for elution predicted by batch measurements.

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