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ION-EXCHANGE BEHAVIOR OR ACTINIDES AND LANTHANIDES

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(Thesis)

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ION-EXCHANGE BEHAVIOR OF ACTINIDES AND LANTHANIDES

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January, 1956

ABSTRACT

The ion-exchange behavior of tripositive plutonium, americium, curium, berkelium, californium, einsteinium, fermium, cerium, promethium, europium, gadolinium, terbium, dysprosium, holmium, thulium, lutetium, and yttrium from Dowex-1 anion-exchange resin with ammonium thiocyanate solutions has been studied. Lanthanides and yttrium elute sooner than actinides under all conditions studied. Neither actinides nor lanthanides showed a simple elution sequence of the members within the series. On elution from Dowex-50 with ammonium thiocyanate the actinides eluted in the usual sequence of decreasing atomic number. The lanthanides studied also exhibited the usual sequence of elution from Dowex-50; however, the actinides eluted sooner than the lanthanides of comparable ionic radius.

The adsorption of lanthanides, americium, and curium on Dowex-50 from low ionic strength perchloric acid solutions was studied at 25° C. The relative adsorbability decreases from lanthanum to dysprosium, but from dysprosium to lutetium, almost no change in adsorbability occurs. Americium and curium adsorb with the same strength as lanthanides of comparable crystallographic radius.

Thermodynamic quantities were evaluated for the adsorption of promethium, thulium, lutetium, and americium by studying the variation of adsorbability at 0°, 25°, and 50° C in weak perchloric acid. The reaction was found to have a considerable ΔC_p effect (C_p = heat capacity at constant pressure). At 25° C the following values were calculated: promethium, $-\Delta F^{\circ} = 3.302$, $\Delta H^{\circ} = 0.88$, $\Delta S^{\circ} = 14.0$; thulium, $-\Delta F^{\circ} = 2.986$, $\Delta H^{\circ} = 1.41$, $\Delta S^{\circ} = 14.7$; lutetium, $-\Delta F^{\circ} = 2.951$, $\Delta H^{\circ} = 1.24$, $\Delta S^{\circ} = 14.0$; and americium, $-\Delta F^{\circ} = 3.305$, $\Delta H^{\circ} = 0.86$, $\Delta S^{\circ} = 14.0$. Free energies and heats are in kilocalories, and entropies are in entropy units.

Relative activity coefficients of very dilute cerous chloride in hydrochloric acid are given for ionic strengths of 0.02 to 0.1. Relative activity coefficients of $M(ClO_4)_3$, where M is a very dilute tripositive actinide or lanthanide ion, in perchloric acid are given for ionic strengths of 0.03 to 0.73.

I. INTRODUCTION

Ion-exchange column elution was first applied to the separation of lanthanide elements by workers on the Manhattan Project.[1] The separation process utilized ammonium citrate solutions as eluant and Dowex-50 as the resin. The same method was used by Cunningham and co-workers to separate americium and curium.[2] This ion-exchange technique, coupled with the hypothesis that the transuranium elements represent a second rare-earth series, was an important factor in the discovery of berkelium, californium, einsteinium, fermium, and mendelevium. The principal point of interest is that the order of elution of both actinides and lanthanides is of decreasing atomic number, which is also taken to be the order of decreasing radius of the hydrated ion. This is true of elution with ammonium citrate,[3-7] ammonium lactate,[7-11] and ammonium alpha-hydroxy isobutyrate[12] from Dowex-50 cation-exchange columns. The elution positions of actinides correspond to the positions of lanthanides with approximately the same ionic radii, i.e., americium elutes near promethium.

In an attempt to find an improved eluant for ion-exchange separations of actinides and lanthanides, Street and Seaborg[13] discovered that 13.3 M HCl produced a separation of americium and curium from promethium and lutetium. Diamond, Street, and Seaborg[14] made a detailed study of tripositive americium, curium, plutonium, lanthanum, cerium, europium, ytterbium, and yttrium by elution from Dowex-50 with hydrochloric acid solutions varying in strength from 3.2 to 12.2 M. It was found that as the hydrochloric acid molarity increased the actinides studied eluted earlier and earlier, but the lanthanides initially eluted earlier, then passed through a minimum at approximately 7 M HCl and began eluting later. In addition, the order of the actinides reversed. Whereas normally the order of elution is curium, americium, and plutonium, in the strongest hydrochloric acid solution the order of elution is plutonium, americium, and curium. This difference in behavior of tripositive actinides and lanthanides was attributed to a difference in complex-ion formability, possibly utilizing f-orbital hybridization in the case of the actinides. Thompson and co-workers[7] extended this work to include berkelium,

californium, einsteinium, and fermium. Also, the behavior of americium, curium, berkelium, californium, einsteinium, and fermium on elution from Dowex-1 anion-exchange resin with 13 M HCl was given. It was found that on elution from Dowex-50 with concentrated hydrochloric acid solution, the order is fermium (einsteinium, californium), berkelium, americium, and curium. Thus, the normal order is exhibited except for americium. With Dowex-1 the order is americium, curium, berkelium (californium, einsteinium), and fermium. The order is the inverse of the normal order on elution from Dowex-50 columns except for americium. In both cases californium and einsteinium were so close in their elution position that it was not possible to tell which preceded the other.

Diamond[15] predicted on the basis of the f-orbital hybridization hypothesis that thiocyanate should complex more strongly with actinides than with lanthanides. Elution of americium and europium from a Dowex-1 anion-exchange column with 4 M NH_4SCN solution proved this prediction true. Europium appeared soon in the eluate while americium appeared much later. It was felt that a detailed study of the behavior of actinides and lanthanides in this system would be of interest from the standpoint of chemical behavior.

Before presenting the experimental work it seems appropriate to discuss some pertinent aspects of ion exchange.

An ion-exchange resin may be thought of as an ionic salt in which one of the ions is permanently attached to an insoluble organic matrix. The charge on the attached ion determines whether the resin is an anion or cation exchanger. In the case of Dowex-50 cation-exchange resin the attached group is sulfonic acid. Dowex-1 anion-exchange resin has a quaternary amine as the attached group. The movable ion associated with the attached group may be any ion of opposite charge.

If the ion-exchange resin is brought into contact with a salt solution the movable cation or anion in the resin phase is displaced by the aqueous cation or anion.

In general the following statements govern the displacement:

a) An ion of higher charge displaces an ion of lower charge from the resin.

b) For similarly charged ions, the ion with smaller (hydrated) radius displaces the ion with larger (hydrated) radius.

c) The displacement occurs according to the law of mass action. Thus, for a cation-exchange resin,

$$MR + A^{+}_{(aq)} = AR + M^{+}_{(aq)} \tag{1}$$

$$Q = (AR)(M^{+})/(A^{+})(MR) \tag{2}$$

where $A^{+}_{(aq)}$ and $M^{+}_{(aq)}$ are singly-charged cations in solution and MR and AR the corresponding resinates. Q is the equilibrium constant and the parentheses represent thermodynamic activities. Similar equations hold for other than singly-charged ions.

If the solution phase contains an anion which complexes with one of the cations a second equilibrium occurs,

$$A^{+}_{(aq)} + C^{-}_{(aq)} = AC_{(aq)} \tag{3}$$

where AC is the complex ion formed. It is easily seen that in addition to the factors given above concerning the displacement reaction, any complex ion formation will also affect the reaction.

An ion-exchange resin column produces an effect similar to a distillation column. A mixture of ions is adsorbed in a narrow band at the top of the column, and a solution is passed through the column. The appearance of the ions in the eluate is dependent on the factors previously discussed.

A theoretical analysis of the ion-exchange column process has been given by Mayer and Tompkins.[16] The relationship between the equilibrium adsorption of an ion and its elution-peak position was shown to be as follows.

Define a quantity K_d as,

$$K_d = [M_r]/[M_s] \tag{4}$$

where $[M_r]$ and $[M_s]$ represent the concentration of an ion in the resin phase and solution phase, respectively, at equilibrium. K_d may be in any units desired, therefore,

$$K_d = M_r/M_s \text{ x(ml of solution/g of resin)} \tag{5}$$

M_r/M_s now represents the distribution of the ion between resin and solution in one theoretical plate of the column.

Finally,

$$C = K_d \times (\text{g of resin/ml of solution}) \qquad (6)$$

where C represents the number of free column volumes which have passed through the resin bed when the ion is at its peak concentration in the eluate. A free-column volume is defined as the amount of solution in the resin bed. The first free-column volume is not included in the calculation, since it provides no fractionation of the ions being separated.

All of the lanthanide and actinide ion-exchange systems which have been studied are those in which considerable complex-ion formation occurs. It is the purpose of this work to investigate one such system which involves thiocyanate as complexing agent and one which involves little or no complexing, namely perchloric acid solutions.

II. EQUILIBRIUM STUDIES WITH AMERICIUM AND EUROPIUM ON DOWEX-1 RESIN AND AMMONIUM THIOCYANATE SOLUTIONS

To begin a study of a new ion-exchange system, it is frequently desirable to do initial studies under equilibrium conditions. With the information obtained it is usually possible to select optimum conditions for ion-exchange column experiments.

A. Experimental

The method used in these experiments consisted of equilibrating solutions of known ammonium thiocyanate concentration with weighed amounts of Dowex-1 resin initially in the chloride form. After the resin was converted to the thiocyanate form, tracer amounts of Am^{241} and $Eu^{154,155}$ were added. The mixture was stirred mechanically until no further change in the tracer ion concentration in solution occurred. The system was then considered to be at equilibrium. The time required to come to equilibrium was approximately two hours. The Am^{241} content was determined by removing an aliquot of the solution, pipetting the aliquot onto a circular platinum plate, drying the plate under an infrared heat lamp, igniting the plate to a dull red heat in a Meker burner flame and then counting the alpha particles emitted by the Am^{241} in a

2π geometry alpha-particle counter. The $Eu^{154,155}$ mixture was determined in a similar manner except that the beta particles emitted were detected by an end-window type Geiger-Müller counter. A thin absorber was placed between the sample and the Geiger-Müller counter to absorb the alpha particles emitted by the Am^{241}. The ammonium thiocyanate concentration was determined by titration with a standard silver nitrate solution.

The Am^{241} used had been produced by neutron irradiation of plutonium. The $Eu^{154,155}$ mixture was obtained from the Oak Ridge National Laboratory. The Dowex-1 resin was 8 percent cross linked, 200 to 400 mesh, having an approximate capacity of 1.2 equivalents per liter of wet resin. Prior to use, the resin was washed alternately with hydrochloric acid, water, ammonium hydroxide, water, perchloric acid, water, hydrochloric acid. It was then oven dried at 110° C overnight. The ammonium thiocyanate used was of CP grade. A special treatment to remove the last traces of iron present in the ammonium thiocyanate solution consisted of adding a small amount of Dowex-1 resin, stirring well for a few minutes and filtering the solution to remove the resin. The $Fe(SCN)_6^{-3}$ complex is adsorbed very strongly by the resin. Distilled water was used throughout. pH was determined by indicator paper (Anachemia Ltd., Montreal, Canada) sensitive to changes of 0.2 of a pH unit. This method of determining pH was used because of the insensitivity of the K_d to changes in pH (see below).

For the measurements at elevated temperatures, a thermostated water bath was employed. The heating unit was composed of a 125-watt knife-blade type heater in series with a Fenwal thermoswitch (Fenwal Inc., Ashland, Massachusetts). This arrangement provided regulation of the bath temperature to ± 0.5° C. An ice bath was employed for the measurements at 0° C.

Unless otherwise stated all experiments were performed in 15-ml centrifuge cones containing 0.500 g of resin and 5.00 ± 0.05 ml of solution.

B. Results

The results of the batch experiments will be given in terms of the "K_d" defined by equation (5). Since only the solution phase is assayed for the tracer ion, the tracer ion present in the resin phase is obtained as the difference between the total amount of tracer ion present and that present in solution at equilibrium. The disintegration rate is proportional to the amount of a radioactive ion; therefore, the expression for K_d becomes,

$$K_d = \frac{c/m_{(total)} - c/m_{(solution)}}{c/m_{(solution)}} \times \frac{\text{ml of solution}}{\text{g of resin}} \qquad (7)$$

where c/m is the disintegration rate in counts/minute.

In Fig. 1 the effect on K_d of varying ammonium thiocyanate concentration is given for americium and europium. This experiment was performed at room temperature and at a pH of 3.5 ± 0.2. The uncertainty in K_d is the statistical standard deviation error calculated from the number of counts recorded.

In Table I the change in K_d with pH is shown for americium in 1 M and 3 M NH_4SCN. The pH was adjusted by adding the required amount of CP grade hydrochloric acid or ammonium hydroxide to the equilibrating solution. The amount of hydrochloric acid or ammonium hydroxide added was not large enough to alter the ammonium thiocyanate concentration appreciably.

Table I

Variation of K_d for Americium with pH

Room Temperature

M NH_4SCN	1			3		
pH	1.6	3.4	6.6	1.9	3.5	5.4
K_d	7 ± 0.5	9 ± 0.9	27 ± 2	49 ± 3	54 ± 4	58 ± 6

The effect of temperature on the K_d of americium was determined in 1 M and 3 M NH_4SCN and for europium in 3 M NH_4SCN at a pH of 3.5 ± 0.2.

The weight of the resin was 0.490 g and 0.110 g for the 1 M and 3 M NH_4SCN solutions, respectively. The results are presented in Fig. 2 for americium and Fig. 3 for europium as a plot of log K_d vs the reciprocal of the absolute temperature. The measurements were made in the order 21°, 51°, 77°, 0° C. The samples were then sealed and, one month later, remeasured at 19°C.

C. Discussion

It is apparent from Fig. 1 that both americium and europium are complexed quite strongly with thiocyanate. If the ratio of K_d's at a given ammonium thiocyanate concentration is taken as a rough measure of the tendency toward complex ion formation, then americium complexes more strongly than europium. It is assumed that only negatively charged ions are adsorbed on the resin.

The linearity of the data plotted in Fig. 1 is due to the fact that only a limited range of thiocyanate concentration was investigated. Consider the reactions involved in the case of americium. First the formation of the negatively charged complex,

$$Am^{+3} + xSCN^- = Am(SCN)_x^{3-x} \tag{8}$$

$$K_1 = (Am(SCN)_x^{3-x})/(SCN^-)^x(Am^{+3}) \tag{8a}$$

Then the adsorption on the resin of the complex ion,

$$Am(SCN)_x^{3-x} + yRSCN = Ry\ Am(SCN)_x + y(SCN^-) \tag{9}$$

$$K_2 = \frac{(Ry\ Am(SCN)_x)(SCN^-)^y}{(RSCN)^y\ (Am(SCN)_x^{3-x})} \tag{9a}$$

Since americium is in tracer concentration no problem arises in evaluating the "(RSCN)" term. $Ry\ Am(SCN)_x \ll RSCN$, so that (RSCN) is constant is arbitrarily set equal to unity. Assume for simplicity that concentration may be substituted for thermodynamic activities. Recalling equation (4),

$$K_d = \frac{[Am(r)]}{[Am(s)]} = \frac{[RyAm(SCN)_x]}{[Am^{+3}] + [Am(SCN)_x^{3-x}]} \tag{10}$$

Substituting from (8a) and (9a) to get our expression in terms of $[SCN^-]$, after simplification, (10) becomes,

$$K_d = \frac{K_1 K_2 [SCN^-]^{x-y}}{1 + K_1 [SCN^-]^x} \qquad (11)$$

Inspection of equation (9) shows that in order to preserve electrical neutrality in the resin, $x - y = 3$. Making this substitution and taking logarithms,

$$\log K_d = \log K_1 K_2 + 3 \log [SCN^-] - \log (1 + K_1 [SCN^-]^x) \qquad (12)$$

Obviously, a plot of $\log K_d$ vs $\log [SCN^-]$ is not linear. The actual situation could be further complicated since it is possible that more than one species of negatively charged complex ion may exist and adsorb on the resin. The presence of positively charged complexes in solution also leads to a more complicated expression for K_d. It is worth noting that when essentially all of the americium is complexed, the third term on the left in equation (11) becomes "$\log K_1 [SCN^-]^x$."

Making this substitution and taking the derivative,

$$\frac{d \log K_d}{d \log [SCN^-]} = 3 - x \qquad (13)$$

This, of course, predicts a linear plot with negative slope numerically equal to the charge on the americium thiocyanate complex ion.

The dissociation constant[17] for thiocyanic acid has been given as 0.14. The data in Table I show that the effect of pH is small, which is to be expected for such a strong acid. The large K_d at a pH of 6.6 in 1 M NH_4SCN may be the result of radiocolloid formation and subsequent adherence to the walls of the equilibrating vessel. This would introduce an error which would make the measured K_d higher than its true value. The trend in the remaining values can be explained on the basis of the difference in thiocyanate ion concentration because of thiocyanic acid formation.

Fig. 2 and Fig. 3 show that the adsorption has an appreciable temperature dependence; also, the europium adsorption seems to be less affected by temperature change than that of americium.

III. ION-EXCHANGE COLUMN ELUTION STUDIES WITH DOWEX-1

A. Experimental

The type of ion-exchange column employed was that described by Thompson, et al.[7] It is essentially a glass tube of 2 to 3 mm diameter, which contains the resin bed, and an outer glass jacket through which vapor or liquid may be circulated for the purpose of temperature control. In these experiments trichloroethylene (bp 87° C) vapor or water from a thermostated bath was used to maintain constant temperature.

Resin for the ion-exchange column bed was prepared from the 200-400 mesh stock by selecting that which settled at a rate of 1/4 to 1/2 cm min^{-1} in water. During the course of the experiment the original supply of resin was exhausted. A new batch of Dowex-1 was obtained, graded, and treated as described previously. The fraction which settled at the rate of 1/4 to 1/2 cm min^{-1} in 1 M HNO_3 was used since it was found that this procedure gave a more uniform particle size distribution.

The pH of the ammonium thiocyanate eluant was that of the solution as prepared. The pH of 0.5 M, 2.0 M, and 4.0 M NH_4SCN was 4.80, 4.48, and 4.21, respectively.

The radioactive properties of the tracer ions studied are listed in Table II. Ce^{144}, Pm^{147}, $Eu^{154,155}$, and Y^{91} were obtained from the Oak Ridge National Laboratory. The Gd^{148} had previously been produced by cyclotron bombardments. Tb^{160}, Dy^{165}, Ho^{166}, Tm^{170}, and Lu^{177} were produced by neutron irradiation of the stable element. Am^{241}, Cm^{242}, Bk^{249}, $Cf^{250,252}$, E^{253}, and Fm^{254} had been produced by neutron irradiation of Pu^{239}.

The procedure in doing an ion-exchange column elution was as follows. The eluant was allowed to flow slowly through the resin bed for several hours at the same temperature as that to be used during the elution. Known amounts of the tracer ions to be studied were combined in a centrifuge cone and evaporated to dryness in a water bath. An air jet into the cone accelerated the evaporation. Then 30 to 60 μl of 4 M NH_4SCN were introduced into the cone and heated in the water bath for a few minutes to dissolve the tracers. The eluant above the resin

Table II

Radioactive Properties of Tracers

Nuclide	Radiation	Energy (Mev)	Half-Life	Ref.
Ce^{144} (Pr^{144})	β^- (β^-)	0.3 (3.0)	282 d (18 min)	a
Pm^{147}	β^-	0.22	2.6 y	a
$Eu^{154,155}$	β^-	1.9, 0.9, 0.6, 0.15, 0.24	16 y, 1.7 y	a
Gd^{148}	α	3.16	>35 y	a
Tb^{160}	β^-	0.9, 0.5, 0.4	73 d	a
Dy^{165}	β^-	1.25	2.3 hr	a
Ho^{166}	β^-	1.84	27 hr	a
Tm^{170}	β^-	0.97, 0.88	129 d	a
Lu^{177}	β^-	0.49, 0.37, 0.17	6.8 d	a
Y^{91}	β^-	1.55	61 d	a
Pu^{239}	α	5.15	24,000 y	a
Am^{241}	α	5.48	475 y	a
Cm^{242}	α	6.10	162 y	a
Bk^{249}	β^-	0.1	~ 1 y	b,c,d
$Cf^{250,252}$	α	6.05, 6.15	12 y, 2 y	b,c,d
E^{253}	α	6.63	20 d	e,f
Fm^{254}	α	7.1	3.2 hr	e,f

a. J. M. Hollander, et. al., Rev. Mod. Phys. 25, 469 (1953).

b. S. G. Thompson, et. al., Phys. Rev. 93, 908 (1954).

c. A. Ghiorso, et al., Phys. Rev. 94, 1081 (1954).

d. H. Diamond, et. al., Phys. Rev. 94, 1083 (1954).

e. B. G. Harvey, et. al., Phys. Rev. 93, 1129 (1954).

f. P. Fields, et. al., Phys. Rev. 94, 209 (1954).

bed was removed, and one drop of 4 M NH_4SCN was allowed to pass into the bed. The solution containing the tracers was placed on top of the bed, and after it passed into the bed, the elution was begun. The purpose in loading the tracers on the ion-exchange column in 4 M NH_4SCN was to ensure that the tracers were adsorbed in a narrow band at the top of the resin bed. When plutonium was to be eluted a slightly different procedure was utilized. The plutonium tracer solution was normally a mixture of (III), (IV), and (VI) valence states. The plutonium tracer was reduced to the (III) state with a small amount of hydrogen iodide, and a 1-μl aliquot of this solution was added to the 4 M NH_4SCN solution containing the other tracers just before loading on the resin bed.

The eluate was collected dropwise on platinium plates, dried under an infrared heat lamp, and ignited to a red heat. The plates were then analyzed for the tracers by counting. Negatron emitters were detected by means of a Geiger counter. The one exception was Bk^{249} whose soft negatron radiation was counted in a windowless proportional counter. Alpha emitters were counted in a 2π geometry alpha-counter or in an alpha pulse height analyzer in which alpha emitters may be identified by the characteristic energies of the alpha particles.

The conditions (ammonium thiocyanate molarity, temperature, and size of resin bed) necessary to elute the tracers at a convenient eluate volume were selected with the aid of equation (6) and the equilibration data of Section II. For this system equation (6) becomes,

$$C = K_d \times 0.9 \qquad (14)$$

Table III shows the agreement between equilibration and column data under various conditions for americium.

Table III

Comparison of Equilibration and Column Data for Americium

$[NH_4SCN]$ $(\frac{moles}{liter})$	Temperature (^oC)	Resin Bed Dimensions Diameter (mm)	Resin Bed Dimensions Length (cm)	Resin Batch	K_d (Am) Equilibration	K_d (Am) Column
2.0	~25	2	14	1	~35	30
0.5	~25	3	4	1	~ 3	2
2.2	33	2	10.5	1	30	24
2.2	87	2	10.5	1	8	6.4
1.1	87	2	10.5	1	1.8	1.5
1.0	33	2	6.5	2	9	10
2.0	87	2	5.9	2	6.6	8
0.96	87	3	5.6	2	1.4	1.0

In order to get symmetrical elution peaks, the elution must be performed slowly enough to enable equilibrium conditions to be reached at all times. At 33° C it was necessary to maintain the eluant flow-rate to less than 0.15 ml/min/cm^2 of resin bed cross-sectional area. At 87° C flow-rates of twice this value were satisfactory.

B. Results and Discussion

Fig. 4 shows a typical elution curve for actinides. This experiment was performed at 87^oC with 2 M NH_4SCN as eluant. The resin was from the second batch, and the resin bed dimensions were 2 mm x 6 cm. Resolution of alpha-emitter elution peaks was accomplished by alpha pulse height analysis. The results of other experiments on actinides are summarized in Table IV. One free column volume has been subtracted. The actinide behavior is depicted somewhat more clearly in Fig. 5 where the elution position is plotted as a function of atomic number.

Table IV

Actinide Elution Peak Positions

$[NH_4SCN]$ $(\frac{moles}{liter})$	Temp. (°C)	Resin Bed Dimensions Dia. (mm)	Length (cm)	Resin Batch	Drop No. to Peak Pu	Am	Cm	Bk	Cf	E	Fm
2.0	~25	2	14	1	-	230	210	-	-	-	-
0.5	~25	3	4	1	-	9	8	-	-	-	-
0.55	~25	3	4	2	-	11	10	-	-	-	-
2.2	33	2	10	1	136	121	109	-	-	-	-
1.0	33	2	7	2	40	37	33	60	67	57	-
2.2	87	2	10	1	35	35	32	-	-	-	-
1.1	87	2	10	1	8	8	7	-	-	-	-
2.0	87	2	6	2	30	28	24	36	41	35	-
0.96	87	2	6	2	-	-	3	5	6	-	-
0.96	87	3	6	2	-	-	5	-	11	9	-
0.96	87	3	6	2	-	6	5	-	11	8	10

Fig. 6 shows a typical elution curve for several lanthanides. This experiment was performed on a 3 mm x 6.5 cm column using 2.0 M NH_4SCN as eluant at a temperature of 33° C. The resin was from the second batch. Resolution of the radioactivity from the several tracer elements was accomplished by an absorption method except for gadolinium which was detected by its alpha activity. The absorption method depends on the fact that the weak promethium negatron particle is easily absorbed. The samples are first counted in the absence of an absorber; then a thin absorber is interposed between sample and detector which reduces the detectable promethium activity essentially to zero, while reducing the activity of cerium and holmium by only a factor of two. The promethium activity may then be obtained by difference. In actual fact it is not the Ce^{144} radiation which is detected primarily when the absorber is interposed, it is the energetic radiation from its Pr^{144} daughter.

It was not possible to determine elution positions for all lanthanides studied in a single experiment because of the difficulty of resolving complex mixtures of negatron emitters. A series of experiments under identical conditions was performed instead. The elution volume of a given lanthanide in the eluate varied somewhat from one experiment to another. It was, therefore, necessary to "normalize" the various experiments before a relative comparison between individual lanthanides could be made. Gadolinium was the principal lanthanide used for normalization. For experiments where gadolinium was absent, either europium or promethium was used as a base for normalization.

Except in the case of promethium the adsorption method for resolving elution peaks is not very satisfactory, especially if the separation between peaks is small.

If two tracer ions are being studied, at least one of which has a half-life conveniently short, their elution peaks may be easily resolved. The eluate samples are first counted soon after the elution is performed. After a time sufficiently long for the short-lived component to be reduced to an insignificant level compared to the long-lived component, the samples are recounted. The short-lived component may then be obtained by difference. If the long-lived component has decayed appreciably, a correction may be applied to determine the amount present during the initial count. This method was used to resolve dysprosium from holmium and europium from terbium. The results of these experiments are presented in Table V. All runs were performed on a 3 mm x 6.5 cm column packed with resin from the second batch using 2.0 M NH_4SCN as eluant at a temperature of 33° C. One free column volume has been subtracted.

Table V

Lanthanide Elution Peak Positions

Experiment	Drop Number to Peak									
	Ce	Pm	Eu	Gd	Tb	Dy	Ho	Tm	Lu	Y
1	12	21	26	-	-	-	-	-	-	-
2	14	21	26	-	-	-	-	23	-	17
5	-	20	-	24	-	23	22	-	-	-
6	12	20	-	-	-	23	22	-	-	-
7	13	18	-	24	-	-	22	-	-	-
8	11	20	-	-	25	-	-	-	-	-
11	10	20	-	-	-	-	-	24	-	-
12	11	-	26	24	26	-	-	-	-	-
13	13	-	27	24	26	-	-	-	-	-
15	-	-	26	24	-	-	-	-	-	-
17	-	20	-	-	-	-	-	-	26	-
18	11	20	-	-	-	-	-	-	30	-

In Fig. 7 the elution positions of lanthanides are plotted as a function of atomic number. Also included for purposes of comparison are the actinide elution positions obtained with 1.0 M NH_4SCN eluant at 33° C from a 2 mm x 7 cm column. Taking into account the difference in column size and molarity of eluant, the actinide positions should be multiplied by a factor of four to provide a more exact comparison to the lanthanide positions. The fermium position is estimated from a separate experiment. The yttrium position is plotted between those of dysprosium and holmium because chemically yttrium resembles those two lanthanides most closely.

Some experiments were performed where both actinides and lanthanides were present. Some typical results are presented in Table VI. Resin from the first batch was used throughout. One free column volume has been subtracted.

Table VI

Actinide and Lanthanide Elution Peak Positions

Exp. No.	M NH_4SCN	Temp. (°C)	Resin Bed Dimensions Diameter (mm)	Length (cm)	Drop Number to Peak Ce	Pm	Eu	Tm	Lu	Y	Am	Cm
1	0.5	~25	3	4	-	-	1±1	-	1±1	-	9	8
2	2.0	~25	2	15.5	17	-	-	-	-	28	260	-
3	2.2	33	2	10	-	14	-	15	-	12	121	109
4	2.5	87	2	10	8	-	-	-	20	-	53	47

It is interesting to compare the results of Table VI with those predicted from the equilibration data. First, assume that the relative elution positions of lanthanides are approximately independent of temperature and molarity of ammonium thiocyanate. That this is true for the actinides may be verified from Fig. 5. From the data in Table V and the positions of lanthanides given in Table VI, the europium peak position should be drop 18 for both experiments 3 and 4. Now the drop number to peak for an ion is directly proportional to its K_d. For experiment 3, the ratio of K_d(Am) to K_d(Eu) is 121/18 = 6.7, and for experiment 4 it is 53/18 = 2.9. From the equilibration data of Section II, the ratios should be 5 and 3.2, respectively. The agreement is considered to be satisfactory. Apparently the change in K_d with temperature is greater for actinides than for lanthanides.

It can be seen from Fig. 7 that neither the actinide nor lanthanide elution positions fall in a simple order of atomic number as is the case in elution from Dowex-50 with most eluants. (The only exception is the plutonium-americium-curium "reversal" with strong hydrochloric acid eluant reported in reference 4.) Comparing homologous members of the two series for which information is available, the same relative order is maintained except for californium and dysprosium. In elution from Dowex-50 yttrium elutes near dysprosium and holmium, but here it elutes much sooner.

If the elution positions were determined solely from ionic radii considerations then the order of elution from Dowex-1 should be just the order of increasing atomic number in both actinide and lanthanide series. Any particular actinide should elute near the lanthanide of similar ionic radius, and yttrium should elute near dysprosium and holmium. This expectation depends on the assumption that only "ionic" complexes with the same charge are formed. If covalent bonding is important in the complex ion, the tendency toward complex ion formation is not necessarily a function of the ionic radii. This might be the explanation of the fact that no simple elution sequence is observed within a series.

There are other indications that complex ion formation in the actinides and lanthanides is not always solely dependent on the ionic radii. Magnusson[18] has measured the distribution of some actinide ions between an aqueous phase (buffered with ammonium chloracetate) and a toluene phase 0.2 M in thenoyltrifluoroacetone. The results are given in terms of "D_a" which is defined as the concentration ratio (toluene/aqueous, volume basis) of the ion studied. Lederer[19] studied the paper chromatography of some lanthanide ions with acetyl acetone as a complexing agent giving the results in terms of an R_f defined as

$$\frac{\text{distance traveled by ion}}{\text{distance traveled by liquid front}} .$$

In Fig. 8 the results of those investigations are compared with the data of Fig. 7. In many respects the shapes of the curves are quite similar.

If certain simplifying assumptions are made, a quantitative estimate of the difference in free energy of formation of the complex ions may be made. Assume that only a single negatively charged species exists and adsorbs on the resin. Because of their similar radii, the complex ions of americium and plutonium should undergo adsorption on the resin to the same extent. From experiment 3 in Table VI, the drop number to peak for promethium is 14, and for americium it is 121. Assume that this difference is entirely due to the difference in the formation constant of the complex ion. With these assumptions,

$$\Delta F^{o}(Pm) - \Delta F^{o}(Am) = RT \ln 121/14 = 1.3 \text{ kcal.} \qquad (15)$$

This is not a large difference in terms of chemical bonding energies. The change in free energy required to make an ion "reverse" its position with respect to another ion is undoubtedly much less, probably of the order of 100 to 300 calories. Considering the energy involved, the tendency of the actinides to form stronger complexes than lanthanides could be due to the greater polarizability of the actinide ions.

It has been pointed out in reference 7 that a number of factors could influence the complex ion formation and elution peak position of an ion. In addition to the ionic radius effect and possible bond hybridization to form covalent complexes, a slight steric hindrance might occur in the formation of higher complexes. There is also the possibility that the (2J + 1) degeneracy of the total angular momentum vector J of the ion might be wholly or partially removed if the surrounding ions produce electric fields not having spherical symmetry. This could lead to changes in entropy the magnitude of which would depend on the term value of the ion and the nature of the field. A satisfactory theory which will explain all the observed facts must await the evaluation of these factors.

The most obvious feature of the foregoing experiment is the difference in group behavior of actinides and lanthanides. It was expected that this would be easily observable in elution from Dowex-50 with ammonium thiocyanate. One might also expect a deviation from the usual monatonic order of elution from Dowex-50, especially for actinides; therefore, some experiments were performed to test these possibilities.

IV. ION EXCHANGE COLUMN ELUTIONS WITH DOWEX-50

A. Experimental

The experimental procedures used in this section are the same as described previously except that the tracers were loaded on the column packed with Dowex-50 resin in 0.05 M HCl rather than in 4 M NH_4SCN. The resin used was the fraction that had a settling rate of 0.5 to 1 cm/min in water.

B. Results and Discussion

The actinide behavior on elution from Dowex-50 is shown in Fig. 9. This experiment was performed at 87° C with 1.8 M NH_4SCN as eluant. The column bed was 2 mm x 4 cm packed with Dowex-50, 4-percent cross-linked resin. The elution order is just the order of decreasing atomic number. Furthermore, curium still preceded americium using 4.4 M NH_4SCN as eluant. No "reversal" of elution peak position, therefore, occurred as would be the case if the relative elution positions from Dowex-50 were just the opposite of those from Dowex-1.

Fig. 10 shows the behavior of americium compared to lutetium, holmium, and promethium. Conditions were the same as above except that the eluant was 2.0 M NH_4SCN. The promethium position was obtained in separate experiments and is indicated by an arrow. Because of the similarity in ionic radii, americium usually elutes near promethium. Here americium elutes considerably sooner, as would be expected if americium complexes more strongly with thiocyanate than does promethium. On elution from Dowex-1 there was a group separation of actinides and lanthanides. In this experiment americium eluted with holmium. This is not in conflict with the idea that the actinides complex more strongly as a group than the lanthanides. The equations involved in the case of Dowex-50 are:

$$M^{+3} + 3NH_4R = MR_3 + 3NH_4^+ \qquad (16)$$

where R represents the immobile resin anion and M^{+3} the actinide or lanthanide ion, and

$$M^{+3} + xSCN^- = M(SCN)_x^{3-x} \qquad (17)$$

Now equation (17) is written identically with equation (8); however, there is one important difference. It was assumed that only negatively charged ions could be adsorbed on the Dowex-1 resin; therefore, the "x" in equation (8) must have a numerical value of four or greater. No such restriction exists for the value of "x" in equation (17). The equilibrium constant of equation (16) is large, and this decreases the M^{+3} concentration in solution and, in turn, the concentration of the complex ion. If the formation of the complex ion occurs stepwise, the adsorption of the $M(SCN)^{+2}$ and $M(SCN)_2^+$ on the resin would tend to decrease further the complex

ion concentration in solution. On the other hand, when Dowex-1 resin is used the formation of the complex ion in solution is favored by its adsorption on the resin. Elution from Dowex-1, therefore, probably gives a more direct measure of the relative strength of complex ion formation, especially of the higher complexes, than does elution from Dowex-50. The implication, of course, is that equation (16) determines to a large extent the elution position of an ion. Under conditions more favorable for complex ion formation (3 M NH_4SCN, 33° C) the order of elution is americium, lutetium, and promethium from Dowex-50, 4-percent cross-linked resin. But if Dowex-50, 12-percent cross-lined resin is used under identical conditions, the order of elution becomes lutetium, americium, and promethium. This "reversal" of americium compared to lutetium can only be attributed to the difference in adsorption on the resin and clearly demonstrates the influence of equation (16) on the relative elution positions. It is not too surprising then that no "reversals" within the series occur on elution from Dowex-50 and that the rather large difference in actinide-lanthanide complexing observed in elution from Dowex-1 becomes less apparent.

V. EQUILIBRIUM ADSORPTION OF LANTHANIDES, AMERICIUM, AND CURIUM ON DOWEX-50

This series of experiments was undertaken to determine the distribution of tracer lanthanides, americium, and curium between Dowex-50 and a low ionic strength solution having no complexing anion present.

A. Adsorption of Cerous Ion from Hydrochloric Acid Solutions

This was a preliminary experiment for the purpose of investigating the feasibility of the proposed measurements.

1. Experimental

Weighed amounts of hydrogen-form, Dowex-50 resin with 4-percent cross-linkage were introduced into double-necked, round-bottomed flasks of 100-ml capacity. A known volume of hydrochloric acid solution containing a known amount of Ce^{144} tracer was introduced into the flasks.

A glass stirring rod was inserted through one of the necks in the flask. The other neck was for the purpose of withdrawing aliquots for analysis.

The flasks were then introduced into a thermostated water bath and stirred mechanically until no further change in the tracer concentration occurred. It was assumed that equilibrium had then been obtained. Additional aliquots were removed for titration with a standard sodium hydroxide solution to determine the acid concentration. The acid concentration was then varied by the addition of either hydrochloric acid or water, and another measurement was made. This procedure allows equilibrium to be approached from either direction, i.e. adsorption or desorption of the tracer.

The resin used was the fraction that settled at the rate of 0.5 to 1 cm/min in water. Treatment prior to use consisted of alternate washes with 4 M NH_4Cl, 1 M, 6 M, and 12 M HCl, and conductivity water. The sample was dried at 110° C until a constant weight was obtained and then it was stored in a desiccator. This single batch was the source of all resin samples. Weighing was done on an Ainsworth Model VM assay balance. A small, ground-glass-stoppered weighing bottle was used, and its weight was determined after each resin sample was removed. The probable error in the weight of each sample was estimated not to exceed 6 μg. Sample weights ranged from 1 to 4 mg. Corrections were applied to get the weight in vacuo.

Solutions were made with CP grade hydrochloric acid and conductivity water (specific conductance, 0.7 to 2 x 10^{-8} mho).

Aliquots of the solution for radioactive assay were taken with a calibrated pipette, usually of nominal 1-ml capacity. At first, there was considerable difficulty in obtaining duplicate samples which gave good agreement, especially at the lowest tracer concentrations. It appeared that very small amounts of resin were in the aliquots. Under the conditions of the experiment, the ratio of tracer on the resin to that in solution was quite high (reaching 10^8 on a volume basis). Therefore, while the amount of resin in the aliquot is insignificant from the standpoint of the volume occupied, its much greater "specific activity" introduces a large error. To prevent the resin from getting

into the aliquot, a small, glass-wool plug was inserted in the capillary tip of a transfer pipette. After the sample was taken, the tip containing the plug was broken off and discarded. Aliquots were then taken from this sample. Preparation of the aliquot for counting has been described in Section II. A windowless proportional counter was employed for counting.

The temperature of the thermostated bath was controlled with a 250-watt, knife-blade heater in conjunction with a mercury thermoregulator (American Instrument Company, Silver Spring, Md.) operating through an electronic relay. The temperature was 24.99 ± 0.01° C and was measured with a thermometer that had been calibrated at the National Bureau of Standards. A Beckmann thermometer showed that the temperature was constant within 0.003° C during the time of the measurements.

2. Results and Discussion

The results of these experiments are given in Table VII. Values of K_d were calculated by equation (7). Fig. 11 shows the variation of K_d with hydrochloric acid concentration. The two points which are quite low on the curve were measured with the sample having the lowest weight of resin. Eventually, however, the same decrease occurred with the other samples. It seems likely that the continued addition of solution had introduced enough impurities to begin altering the resin phase. The equivalent weight of the dry, hydrogen-form resin was found to be 199 by titration with sodium hydroxide. A 1-mg sample would, therefore, have a capacity of 5 microequivalent weights. For example, 45 μg of trivalent aluminum would use up all the available resin sites, and very little adsorption of the trivalent cerium tracer would occur. The points at the lowest ($\leq$ 0.02 M) hydrochloric acid concentrations are not very reliable because the aliquots had counting rates that were too low for an accurate determination.

The time required to reach equilibrium from the initial addition of the solution was found to be 3 hr for the samples that were 0.05 and 0.1 M in hydrochloric acid. The fact that the data in Fig. 11 fell on a smooth curve and were obtained by approaching equilibrium from either direction shows that the system is reversible.

Table VII

Adsorption of Cerous Ion

Exp. No.	Resin (mg)	HCl Conc. ($\underline{M} \times 10^2$)	Volume of Solution (ml)	Total Ce(III) ($c/m \times 10^{-7}$)	Ce(III) ($c/m\ ml^{-1}$)	K_d
1	1.02	1.28	25	1.20	49	240×10^6
		1.53	26	1.18	75	155×10^6
		1.60	25	1.09	85	126×10^6
		3.25	25	1.08	847	12.5×10^6
		5.22	30	1.06	4450	2.32×10^6
2	2.15	10.13	25	1.21	1.18×10^4	4.66×10^5
		4.96	39	1.17	1060	50.5×10^5
		3.66	39	1.16	404	134×10^5
		3.74	41	1.08	437	114×10^5
		2.32	42	1.055	98	500×10^5
3	4.384	5.10	25	3.14	1610	44.4×10^5
		7.64	39	3.09	5840	12.0×10^5
		11.39	36	3.05	2.23×10^4	3.04×10^5
		9.16	39	2.755	1.01×10^4	6.12×10^5
		6.75	39	2.72	3610	17.1×10^5
		3.78	40	2.705	513	120×10^5
4	1.24	2.56	25	1.19	264	3.63×10^7
		1.67	30	1.18	71	13.4×10^7

B. Adsorption of Lanthanides, Americium, and Curium from 0.110 M Perchloric Acid

1. Experimental

On the basis of information obtained from the preliminary experiment and for convenience, certain changes were made in the experimental procedure. Instead of the round-bottomed flasks, 10-ml volumetric flasks with ground-glass stoppers were used. After the introduction of the sample, the flasks were sealed with paraffin wax and placed on a wheel which rotated in the thermostated bath. Although equilibrium was obtained in less than 4 hr, the samples were usually not removed before 24 hr of agitation.

The radioactive tracers were La^{140}, Ce^{144}, Pr^{142}, Nd^{147}, Pm^{147}, Sm^{153}, $Eu^{154,155}$, $Gd^{153,159}$, Tb^{160}, Dy^{165}, Ho^{166}, $Er^{169,171}$, Tm^{170}, $Yb^{169,175}$, Lu^{177}, Am^{241}, and Cm^{242}. The cerium, promethium, europium, terbium, americium, and curium were available from previous experiments. The remaining activities were produced by neutron irradiation of microgram amounts of the stable isotopes in the Materials Testing Reactor (Arco, Idaho) with the exception of Dy^{165} which was produced in the Livermore reactor (University of California Radiation Laboratory, Livermore, California).

Following irradiation, the activities were purified by a Dowex-50 ion-exchange column utilizing ammonium alpha-hydroxy isobutyrate as eluant. Conditions for the particular separation to be made were selected from the data of reference 12. A typical separation is shown in Fig. 12. In this case, neodymium was irradiated. The promethium activity is due principally to Pm^{149} which is the daughter of Nd^{149}. The Pr^{142} and Sm^{153} activities resulted from neutron capture by the stable isotopes of those elements present as an impurity in the neodymium. The first peak is due to an unidentified activity which is always present after irradiation. It passes immediately through the column with the 0.05 M HCl used for loading the activities to be separated. This means that it is not adsorbed on the Dowex-50 resin and is a very undesirable contaminant. Identification of the activity following separation was made either by a previous knowledge of its

elution peak position or by its characteristic nuclear properties, i.e. half-life or maximum negatron energy.

The need for high-purity conditions has already been pointed out. Spectrographic analyses were performed to determine the amounts of impurities from various sources in the sample. Some representative results are given in Table VIII and are normalized to the amount of impurity in a single sample. The mass of stable isotopes in the tracers varied from 6 μg for europium to 0.003 μg for terbium, again on the basis of the amount in a single sample. As an added precaution against the introduction of impurities into the system, the glassware used in the experiments was boiled for 1 hr in concentrated nitric acid. It is estimated that at least 98 percent of the resin remained in the hydrogen form.

Table VIII

Spectrographic Analyses

Sample	Impurity (μg)				
	Al	Ca	Fe	Mg	Na
Water	ND*	0.1	ND	0.1	ND
Perchloric Acid	ND	ND	ND	ND	ND
Dowex-50	ND	ND	ND	ND	ND
Cerium Tracer	0.05	0.3	ND	0.02	ND
Neodymium Tracer	0.05	0.05	0.05	0.03	ND

*ND signifies that the impurity is below the level of sensitivity for detection (0.01 μg).

Because of the tendency of cerium (III) to form a chloride complex, even in low strength solution,[20] it was decided to use perchloric rather than hydrochloric acid.

The primary standard for hydrogen-ion determination was hydrochloric acid which was analyzed gravimetrically by silver chloride precipitation. The sample to be analyzed was neutralized with excess sodium hydroxide and back-titrated with hydrochloric acid using methyl-red indicator.

The titration was completed at an elevated temperature (to expel carbon dioxide). Both the sodium hydroxide and hydrochloric acid solutions were frequently checked against each other and against the primary standard. The maximum deviation of duplicate analyses rarely exceeded 0.2 percent. It was found that each sample did not have to be analyzed after equilibration, only the stock solution from which the samples were prepared.

All aliquots for radiometric analysis were counted in a windowless proportional counter except americium and curium which were counted on a 2π geometry alpha counter. Usually the procedure was to count the aliquots from the stock solutions and then the aliquots from the solution after equilibration. Some of the activities had such short half-lives that appreciable decay occurred during the counting time. In these cases two counters were used, one containing the initial assay, the other containing the assay after equilibration. By counting both during the same time interval no correction for decay was needed.

During the course of these experiments the temperature of the thermostated bath gradually decreased. The average temperature was $24.98 \pm 0.03^{\circ}$ C.

2. Results and Discussion

Table IX summarizes the results of the experiments. The last column in the table is the correction of the observed K_d to the K_d in 0.110 M $HClO_4$. Several of the determinations on a single ion (cerium, promethium, europium, thulium, lutetium) were performed twice, using different amounts of tracer and at widely spaced time intervals. The difference in two separate experiments amounted to slightly over 3 percent in the worst case.

Table IX

Adsorption of Tripositive Lanthanides, Americium, and Curium

The solution volume was 10 ml. The initial concentration in c/m of tracer per milliliter is C_o and the final concentration, C_s.

Ion	$HClO_4$ Conc. (M)	Resin Weight (mg)	$C_o x10^{-5}$	$C_s x10^{-3}$	$K_d x10^{-5}$	$K_d \times 10^{-5} \times \left(\frac{M\ HClO_4}{0.110}\right)^3$
La	0.1110	1.610	0.574	0.851	4.12	4.28
	0.1110	1.875	0.561	0.704	4.20	4.33
Ce	0.1102	2.742	1.002	0.810	4.47	4.49
	0.1102	2.192	1.017	1.021	4.50	4.52
*	0.1115	2.668	3.182	1.584	4.22	4.38
*	0.1115	1.557	3.182	2.226	4.23	4.40
	0.1099	2.539	3.346	2.960	4.41	4.40
	0.1099	3.112	3.346	2.471	4.32	4.31
Pr	0.1110	2.843	5.344	4.979	3.74	3.84
	0.1110	3.048	5.302	4.532	3.81	3.91
Nd	0.1112	1.632	0.472	0.787	3.61	3.73
	0.1112	1.481	0.468	0.839	3.70	3.82
Pm	0.1102	3.179	1.005	0.848	3.70	3.72
	0.1102	2.416	1.005	1.089	3.78	3.80
	0.1099	3.809	3.382	3.294	3.84	3.83
	0.1099	3.906	3.382	2.207	3.90	3.89
	0.1099	1.429	3.382	6.326	3.67	3.66
Sm	0.1110	2.375	2.112	2.762	3.18	3.26
	0.1110	2.058	2.086	3.135	3.19	3.27
	0.1110	2.883	2.059	2.184	3.24	3.32

Table IX (Continued)

Ion	$HClO_4$ Conc. (M)	Resin Weight (mg)	$C_o x10^{-5}$	$C_s x10^{-3}$	$K_d x10^{-5}$	$K_d \times 10^{-5} \times \left(\frac{M\ HClO_4}{0.110}\right)^3$
Eu	0.1102	1.844	0.653	1.108	3.14	3.16
	0.1102	2.379	0.653	0.815	3.33	3.35
	0.1099	2.460	5.026	6.488	3.11	3.10
	0.1099	4.117	5.004	3.605	3.315	3.34
	0.1099	3.463	5.004	4.472	3.20	3.19
Gd	0.1110	2.336	7.99	12.95	2.63	2.70
	0.1110	2.824	7.90	10.28	2.68	2.75
Tb	0.1102	2.310	0.255	0.395	2.75	2.76
	0.1102	4.242	0.255	0.220	2.71	2.72
Dy	0.1110	1.732	1.126	2.740	2.32	2.38
	0.1110	2.618	0.842	1.361	2.33	2.39
	0.1110	2.250	0.684	1.309	2.28	2.34
Ho	0.1110	2.016	5.160	11.64	2.15	2.21
	0.1110	2.420	5.104	9.38	2.21	2.27
	0.1110	2.162	5.046	10.34	2.21	2.27
Er	0.1110	2.661	1.637	2.770	2.17	2.23
	0.1110	1.400	1.614	5.234	2.13	2.18
Tm	0.1112	2.634	1.384	1.202	2.16	2.23
	0.1112	2.603	1.358	2.332	2.20	2.27
	0.1112	1.862	1.358	3.330	2.14	2.19
	0.1098	1.758	4.280	10.82	2.20	2.21
	0.1098	2.985	4.270	6.37	2.21	2.20
Yb	0.1108	1.982	0.600	1.375	2.17	2.21
	0.1108	2.542	0.600	1.052	2.20	2.24

Table IX (Continued)

Ion	$HClO_4$ Conc. (M)	Resin Weight (mg)	$C_o x10^{-5}$	$C_s x10^{-3}$	$K_d x10^{-5}$	$K_d \times 10^{-5} \times \left(\frac{M\ HClO_4}{0.110}\right)^3$
Lu	0.1112	1.643	1.180	3.488	2.01	2.08
	0.1112	2.606	1.180	2.130	2.08	2.15
	0.1098	1.982	0.568	1.347	2.04	2.03
	0.1098	2.451	0.460	0.879	2.09	2.08
Am	0.1102	1.945	1.747	2.350	3.77	3.78
*	0.1102	2.435	1.747	1.868	3.80	3.81
†	0.1102	2.346	1.747	0.580	3.84	3.85
Cm	0.1102	2.592	0.475	0.496	3.65	3.65
*	0.1102	1.844	0.475	0.357	3.57	3.57
†	0.1102	1.451	0.475	0.269	3.62	3.62

* 5-ml solution.

† 3-ml solution, measured in Teflon container.

Fig. 13 is a plot of log K_{d_o} (average of K_d's in 0.110 M $HClO_4$) against the crystallographic radii of the ions, which is almost equivalent to plotting against the atomic number. The crystallographic radii of the lanthanides are those given by Templeton.[21] The radius of americium is taken as 1.00 Å[22] and that of curium as 0.99 Å.[23] The reason for plotting in this manner is as follows. Ion exchange is primarily the result of an electrostatic interaction. On a simple basis, then, the free energy of adsorption should be a linear function of the reciprocal of the radius of the ion, if like charges are compared. The radius must be that of the hydrated ion. In the absence of quantitative data on the hydrated radii, it will be assumed that the hydrated radius is inversely proportional to the crystallographic radius.[24] Log K_d is proportional to the free energy of adsorption.

The curve shows an interesting feature. In going from lanthanum to dysprosium a gradual decrease in K_d is observed, as expected. But from dysprosium to lutetium there is almost no decrease at all. While the scatter of the experimental points from the curve appears to be somewhat greater than could reasonably be expected, this effect is undoubtedly real. The equation for the reaction studied can be written as,

$$M(H_2O)_a^{+3} + 3H(H_2O)_bR = M(H_2O)_cR_3 + 3H(H_2O)_d^{+} + (a + b - c - d)H_2O \qquad (18)$$

taking into account the decrease in hydration of the ion when it is adsorbed on the resin. If a change in the average number of hydration waters occurred in the neighborhood of dysprosium, such a curve might result. For, in that case, the crystallographic radius would no longer be proportional to the hydrated radius all along the curve. The lanthanides heavier than dysprosium, having fewer waters of hydration than the lighter lanthanides, would appear to adsorb too strongly on a relative basis. This discontinuity in the neighborhood of dysprosium (actually the discontinuity occurs between terbium and dysprosium) can also be observed in the ΔF^o and ΔH^o of M^{+3}(aq.), the ΔH^o of MCl_3(aq.), and in the ΔF^o of $M(OH)_3$ and $M_2(SO_4)_3 \cdot 8H_2O$[25] (where M^{+3} is the lanthanide ion) if those quantities are plotted against the crystallographic radii of the ions. It should be mentioned that the reliability of all the quantities cited depends on the reliability of the measurements made on the metals. A systematic error in that single measurement would be reflected in each of the other measurements. Also the crystallographic radii exhibit a slight discontinuity (with atomic number) at gadolinium, rather than dysprosium.

C. Temperature Dependence of Adsorption

No data exist in the literature for the temperature dependence of the adsorption of lanthanides or actinides on Dowex-50. In this study the adsorption of promethium, lutetium, thulium, and americium was determined at 0°, 25°, and 50^oC.

1. Experimental

The experimental method was essentially the same as in the preceding section. It was found necessary to preheat or precool (for 50° C and 0° C, respectively) the volumetric flasks before sealing with paraffin to prevent leakage out of or into the flasks. Titrations for hydrogen ion were necessary for each sample at 0° C because of the possibility of leakage into the flask.

The thermostated bath was used for the measurements at 25° and 50° C.

The measurements at 0° C were performed by placing the samples in a Dewar flask to which was added finely divided ice made from distilled water and chilled distilled water. The Dewar flask, after being tightly stoppered, was rotated for 24 hr. More ice was added as needed. The temperatures at 0° C and 50° C were determined to 0.01° C. Measurements were made at all three temperatures on some samples, and at least two samples of each ion were measured at two temperatures.

2. Results and Calculations

The results are summarized in Table X.

Table X

Adsorption at 50° and 0° C

(Data for 25° C included in Table IX)

Ion	$HClO_4$ Conc. (M)	Temp. (°C)	Resin Weight (mg)	$C_o x10^{-5}$	$C_s x10^{-3}$	$K_d x10^{-5}$	$K_{d_o} \times 10^{-5}$
Lu	0.1097	0	1.982	0.338	0.851	1.95	1.94
	0.1098	0	2.451	0.307	0.617	1.98	1.97
*	0.1013	0	2.377	0.374	0.603	2.57	2.01
	0.1097	49.53	2.329	0.719	1.194	2.54	2.52
	0.1098	49.53	2.377	0.656	1.098	2.47	2.46
	0.1098	49.53	2.507	0.634	0.996	2.50	2.49
	0.1098	49.53	2.451	0.591	0.964	2.46	2.45

Table X (Continued)

Ion	$HClO_4$ Conc. (M)	Temp. (°C)	Resin Weight	$C_o x10^{-5}$	$C_s x10^{-3}$	$K_d x10^{-5}$	$K_{d_o} \times 10^{-5}$
Tm	0.1096	0	2.116	4.234	9.340	2.10	2.08
	0.1097	0	1.758	4.192	11.400	2.04	2.02
	0.1098	0	2.985	4.186	6.780	2.03	2.02
	0.1098	49.53	3.217	4.380	4.951	2.72	2.71
	0.1098	49.53	2.116	4.360	7.514	2.70	2.69
	0.1098	49.53	2.686	4.360	6.027	2.66	2.65
	0.1098	49.53	2.985	4.350	5.367	2.68	2.67
Pm	0.1099	0	3.809	3.300	2.218	3.88	3.88
	0.1099	0	3.906	3.300	2.144	3.80	3.80
	0.1099	48.20	3.809	3.274	1.976	4.28	4.28
	0.1099	48.20	3.906	3.274	1.890	4.34	4.34
Am	0.1100	0	2.098	4.115	4.963	3.91	3.91
	0.1098	0	2.188	4.115	4.800	3.86	3.84
†	0.1100	24.98	2.319	4.115	4.498	3.80	3.80
†	0.1100	24.98	2.098	4.115	5.023	3.78	3.78
†	0.1100	24.98	2.188	4.115	4.783	3.81	3.81
	0.1100	48.20	2.098	4.115	4.460	4.34	4.34
	0.1100	48.20	2.188	4.115	4.228	4.36	4.36
	0.1100	48.20	2.319	4.115	4.047	4.31	4.31

* Some leakage from the bath water into the equilibration vessel occurred.

† These data were not included in Table IX.

The equation for the reaction is

$$M^{+3} + 3HR = MR_3 + 3H^+ \tag{19}$$

$$K = \frac{(MR_3)(H^+)^3}{(HR)^3(M^{+3})} = \frac{[MR_3][H^+]^3\gamma_{MR}\gamma^3_{H^+}}{[HR]^3[M^{+3}]\gamma^3_{HR}\gamma_{M^{+3}}} \tag{19a}$$

where γ is the activity coefficient in the phase indicated. Since HR does not change when tracers are employed, $(HR)^3$ is unity. The resin phase activity coefficients are not known and will arbitrarily be set equal to unity. This is equivalent to choosing a standard state.

$$K = \frac{[MR_3][H^+]^3\gamma^3_{H^+}}{[M^{+3}]\gamma_{M^{+3}}} = cK_{d_o}\frac{[H^+]^3\gamma^3_{H^+}}{\gamma_{M^{+3}}} \tag{20}$$

where "c" is a constant of proportionality to transform the K_{d_o} to an equivalent basis. Its value is 0.199. $[H^+]$ is now fixed to the value at which K_{d_o} was determined. Then,

$$-\Delta F^o = RT \ln K = 4.57T \log 0.199 \cdot K_{d_o} \frac{[H^+]^3\gamma^3_{H^+}}{\gamma_{M+3}} \tag{21}$$

The work of Spedding[26] shows that the activity coefficients of the lanthanide chlorides have the same value at a given μ (ionic strength) up to a μ of 0.2 at least. In this experiment μ was 0.11; therefore, it is assumed that γ_{M+3} will be the same for all M^{+3} ions. Since all M^{+3} ions are in tracer concentration the γ_{H^+} will be that of the pure solution. For the evaluation of the activity coefficients the compilation of Kielland[27] for the individual ion was used. A correction for the variation of activity coefficient with temperature was applied.[28] Finally,

$$-\Delta F^o = 4.57T \log \alpha K_{d_o} x\ 10^{-4} \tag{22}$$

where α has the value 6.73, 7.00, and 7.42 at 0°, 25°, and 50° C, respectively.

The ΔF^o's calculated by equation (23) are shown in Table XI. Because the elevated temperature was not exactly 50° C a linear correction in α was made.

Table XI

Free Energy of Adsorption

Ion	T (^{o}K)	α	K_{d_o} x10^{-4}	log αK_{d_o} x 10^{-4}	4.57T x 10^{-3}	$-\Delta F^{o}$ (kcal)
Lu	273.2	6.73	19.7	2.122	1.248	2.648
	298.2	7.00	20.9	2.165	1.363	2.951
	322.7	7.41	24.8	2.264	1.475	3.339
Tm	273.2	6.73	20.3	2.135	1.248	2.664
	298.2	7.00	22.2	2.191	1.363	2.986
	322.7	7.41	26.8	2.298	1.475	3.390
Pm	273.2	6.73	38.4	2.412	1.248	3.010
	298.2	7.00	37.8	2.423	1.363	3.302
	321.4	7.39	43.1	2.503	1.469	3.677
Am	273.2	6.73	38.8	2.417	1.248	3.016
	298.2	7.00	38.0	2.425	1.363	3.305
	321.4	7.39	43.4	2.506	1.469	3.681

A plot of log αK_{d_o} against the reciprocal of the absolute temperature should have a slope of $-\Delta H^{o}/4.57$ where ΔH^{o} is the heat of reaction. Such a plot did not give a linear relationship indicating a considerable ΔC_p (C_p is heat capacity at constant pressure) effect. It was, therefore, necessary to use the relationships,[29]

$$\Delta F^{o} = \Delta H_o - \Delta C_p T \ln T + IT \qquad (23)$$

and

$$\Delta H^{o} = \Delta H_o + \Delta C_p T \qquad (24)$$

where ΔH_o, ΔC_p, and I are constants which may be evaluated by solving equation (23) as a simultaneous set of equations using the data of Table XI. Once the constants are evaluated, equation (24) may be used to calculate the ΔH^{o} of the reaction. The ΔS^{o} may then be calculated through the relationship

$$\Delta F^{o} = \Delta H^{o} - T\Delta S^{o} \qquad (25)$$

where ΔS^{o} is the entropy change.

The constants in the equation for each ion that result from solving equation (23) are given in Table XII. The thermodynamic quantities obtained by solving equations (24) and (25) are also given.

Table XII

Heat and Entropy of Adsorption

Ion	Constants of Equation (24) $-\Delta H_o$	ΔC_p	I	$-\Delta F^o_{298}$ (kcal)	ΔH^o_{298} (kcal)	ΔS^o_{298} (e.u.)
Lu	12098	44.71	285.5	2.951	1.24	14.0
Tm	11495	43.27	275.1	2.986	1.41	14.7
Pm	15412	54.63	352.0	3.302	0.88	14.0
Am	16012	56.58	365.1	3.305	0.86	14.0

3. Discussion

Table XII is somewhat misleading in that no error limit has been set on the values. Now the accuracy of ΔH^o is dependent ultimately on the accuracy with which the ΔF^o can be measured. If one assumes a probable error of 1 percent in K_{d_o} then the probable error in evaluating the ΔC_p is approximately 17 percent. Now this error is compensated for in equation (23) because here I is determined almost entirely by the value of ΔC_p. Thus the relative value of ΔH_o will also be quite good. In evaluating ΔH^o by equation (24) the inherent error in ΔC_p is not entirely compensated for; but even for a large error in K_{d_o}, the ΔH^o should not be in error by more than 10 percent. The error in ΔS^o is more dependent on the error in ΔF^o than that in ΔH^o in this system. A reasonable estimate of the error in ΔS^o would be 5 percent or less.

There is one objection in the evaluation of ΔS^o. In deriving equation (22), one of the implied assumptions was that a reference state was chosen in which all M(III) ions would have the same thermodynamic activity, i.e. a resin phase which is essentially all in the hydrogen form. This means that the resin phase activity coefficients are

identical for different M(III) ions. Now the resin phase may be thought of as a concentrated ionic solution having a $\mu \simeq 2.5$. (The hydrogen form resin has a capacity of 5 equivalents per 1000 g of dry resin, and water absorption increases the volume by a factor of two.) It could hardly be expected that the M(III) ions would all have the same activity coefficients. It is possible to make a crude guess as to how much difference there would be in the activity coefficients. The activity coefficients of aqueous $NdCl_3$ and YCl_3 at an ionic strength of 2.4 are 0.289 and 0.309.[30] Assuming that this ratio is the same as the ratio of resin phase activity coefficients and that the activity coefficient of neodymium is the same as those of americium and promethium and that of yttrium is the same as those of thulium and lutetium, a difference in ΔF^{o}_{209} of 0.041 kcal could be expected. This amounts to a difference of only 2 percent in the relative ΔF^{o}, which would also appear in ΔS^{o} but not in ΔH^{o}.

It is fortuitous that the ΔS^{o} of americium, promethium, and lutetium are all the same at 25° C. At 0° C the difference in ΔS^{o} of americium and lutetium amounts to 1 e.u. This difference is a consequence of the apparently different ΔC_p's. While these data are not extensive enough or precise enough to say that this is a real effect, they give a strong indication; especially since the ΔC_p's of both americium and promethium are approximately 55 while those of both lutetium and thulium are approximately 44. Thus in Fig. 9 americium and promethium lie on one section of the curve while thulium and lutetium lie on a different section of the curve. This might be interpreted as evidence that a different amount of coordinated water is lost on adsorption of the ions on one section of the curve with respect to the amount lost by the ions on the other section. At any rate it seems evident that further work would prove fruitful in resolving these possibilities.

D. Relative Activity Coefficients

By studying the variation of K_d of tracer ions with concentration of acid the relative activity coefficients of the ions may be determined.[20] From equation (20),

$$K = \frac{K_d[H^+]^3\gamma^3_{\pm H^+}}{\gamma_{+M^{+3}}} \tag{26}$$

Multiplying denominator and numerator on the right by γ^3-A, where A is the particular anion studied,

$$K = \frac{K_d[H^+]^3\gamma^6_{\pm HA}}{\gamma^4_{\pm MA_3}} \tag{27}$$

or,

$$K\gamma^4_{\pm MA_3} = K_d[H^+]^3\gamma^6_{\pm HA} \tag{27a}$$

Since the M^{+3} is in tracer concentration, $\gamma_{\pm HA}$ will be that of the pure acid. Thus, all the terms on the right may be measured or are known. $K^{1/4}\gamma_{\pm MA_3}$ is then a relative measure of the activity coefficient of the very dilute M^{+3} in a solution of HA.

1. Experimental

The experimental method was the same as was described in the preceding sections.

The cerous and curium stock solutions were initially 0.02 M in perchloric acid. After the solution was introduced into the equilibration vessel, the perchloric acid concentration was adjusted by adding the required amount of concentrated perchloric acid. The samarium and holmium samples were those used previously to obtain the data in Table IX. After equilibration, each sample was titrated to determine the exact perchloric acid concentration. Molarities were changed to molalities by the usual method.

2. Results and Calculations

Table XIII gives the results of the experiments. In Table XIV the details of the calculation of $K^{1/4}\gamma_{\pm MA_3}$ are given. The data for cerium in hydrochloric acid were obtained by constructing a plot of log K_d versus log mHCl using the data in Table VII. A smooth curve was drawn through the experimental points, and values of K_d at the chosen hydrochloric acid molalities read from the smooth curve.

The values of $K\gamma^4_{\pm M(ClO_4)_3}$ were all "normalized" to cerium. The normalization was accomplished by constructing the same type of plot as for cerium in hydrochloric acid. At a perchloric acid concentration where all four curves overlapped, values of K_d for each ion were read off the plot. Then the values of $K\gamma^4_{\pm M(ClO_4)_3}$ for each ion were multiplied by the ratio $K_d(Ce)/K_d(ion)$. The values which resulted are given in Table XIV as $K(Ce)\gamma^4_{\pm M(ClO_4)_3}$. The values in the last column in Table XIV are the relative activity coefficients, $K^{1/4}(Ce)\gamma_{\pm M(ClO_4)_3}$. Assuming that all M^{+3} ions have the same relative activity coefficients in the concentration range studied then $K^{1/4}(Ce)\gamma_{\pm M(ClO_4)_3}$ becomes $K^{1/4}(Ce)\gamma_{\pm Ce(ClO_4)_3}$. Within the error of the experiments, this is a good approximation.

Fig. 14 is a plot of log (relative activity coefficient) as a function of $m^{1/2}$ where m is the molality of the acid. Also included are the relative activity coefficients of $Ce(ClO_4)_3$ given in reference 20. The values of the relative activity coefficient in reference 20 differ numerically from those given in this work, and it was necessary to apply a correction factor so that a direct comparison could be made. Because the cerium and curium were measured at very nearly the same molality of perchloric acid and the values of $K^{1/4}(Ce)\gamma_{\pm M(ClO_4)_3}$ were essentially identical only the values for cerium are plotted.

The slope at the lowest ionic strength is still considerably less than the theoretical slope from Debye-Hückel theory for 3-1 type electrolytes.

Table XIII

Adsorption from Perchloric Acid Solutions

C_o is the total amount of ion present (c/m). C_s is the same as in Table IX.

Ion	$HClO_4$ Conc. (M)	Resin Weight (mg)	Solution Volume (ml)	$C_o \times 10^{-6}$	$C_s \times 10^{-3}$	$K_d \times 10^{-4}$
Ce	0.0308	1.733	10	6.69	0.156	2470
	0.0616	2.431	10	6.69	0.981	280
	0.0764	2.748	10	6.69	1.790	136
	0.1186	2.844	10	6.69	7.010	33.2
Cm	0.0307	1.950	10	15.61	0.382	2100
	0.0618	2.638	10	15.61	2.522	234
	0.0772	2.787	10	15.61	4.915	114
	0.1196	3.007	10	15.61	18.51	27.2
Ho	0.1148	-	-	-	-	22.5
	0.2937	2.016	7.7	0.689	26.31	0.917
	0.7289	2.420	7.7	0.639	70.21	0.058
Sm	0.1148	-	-	-	-	32.8
	0.2037	2.375	7.4	0.767	6.886	4.38
	0.5050	2.883	7.9	0.564	37.29	0.251

Table XIV

Relative Activity Coefficients

Cerous Chloride in Hydrochloric Acid

M	$K_d \times 10^{-6}$	$\gamma_{\pm HCl}(31)$	$K\gamma^4_{\pm CeCl_3}$	$K^{1/4}\gamma_{\pm CeCl_3}$
0.02	74	0.875	266	4.04
0.03	23.5	0.855	248	3.96
0.05	4.75	0.830	194	3.73
0.10	0.48	0.796	122	3.32

$M(ClO_4)_3$ in Perchloric Acid*

Ion	M	$K_d x 10^{-4}$	$\gamma_{\pm HClO_4}$†	$K\gamma^4_{\pm M(ClO_4)_3}$	$K(Ce)\gamma^4_{\pm M(ClO_4)_3}$	$K^{1/4}(Ce)\gamma_{\pm M(ClO_4)_3}$
Ce	0.0308	2470	0.859	290	290	4.12
	0.0616	280	0.825	206	206	3.79
	0.0764	136	0.813	175	175	3.63
	0.1186	33.2	0.797	142	142	3.45
Cm	0.0307	2100	0.859	244	288	4.12
	0.0618	234	0.825	174	205	3.78
	0.0772	114	0.812	149	176	3.65
	0.1196	27.2	0.797	119	140	3.44
Ho	0.1148	22.5	0.798	87.9	144	3.46
	0.2937	0.917	0.768	47.6	78	2.97
	0.7289	0.058	0.788	53.7	88	3.06
Sm	0.1148	32.8	0.798	128	144	3.46
	0.2037	4.38	0.777	81.4	91	3.09
	0.5050	0.251	0.769	66.9	75	2.94

*Part of these data were obtained in collaboration with Dr. G. R. Choppin.

†Reference 32.

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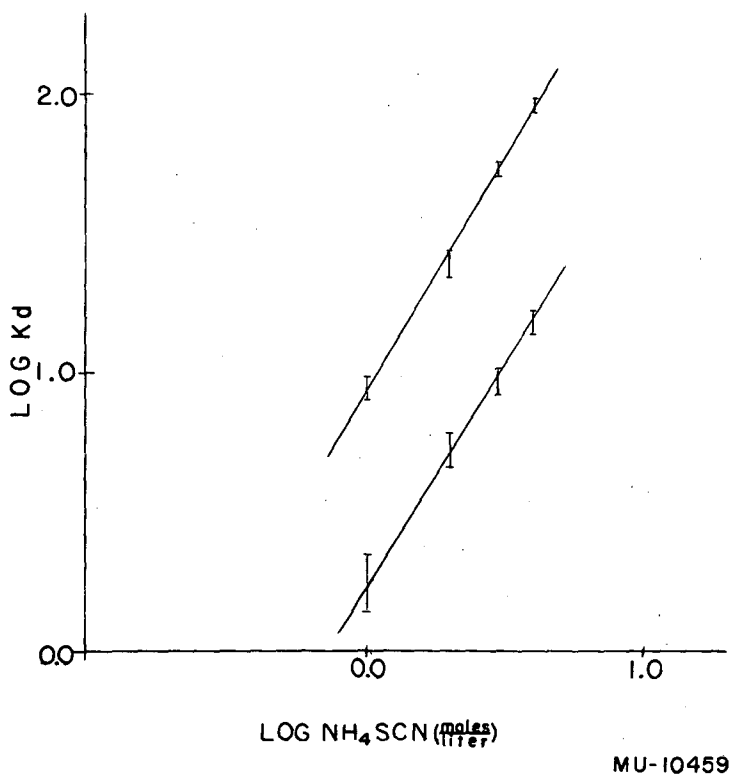

Fig. 1 Logarithm of K_d vs. logarithm of ammonium thiocyanate concentration. Upper curve is americium, lower is europium.

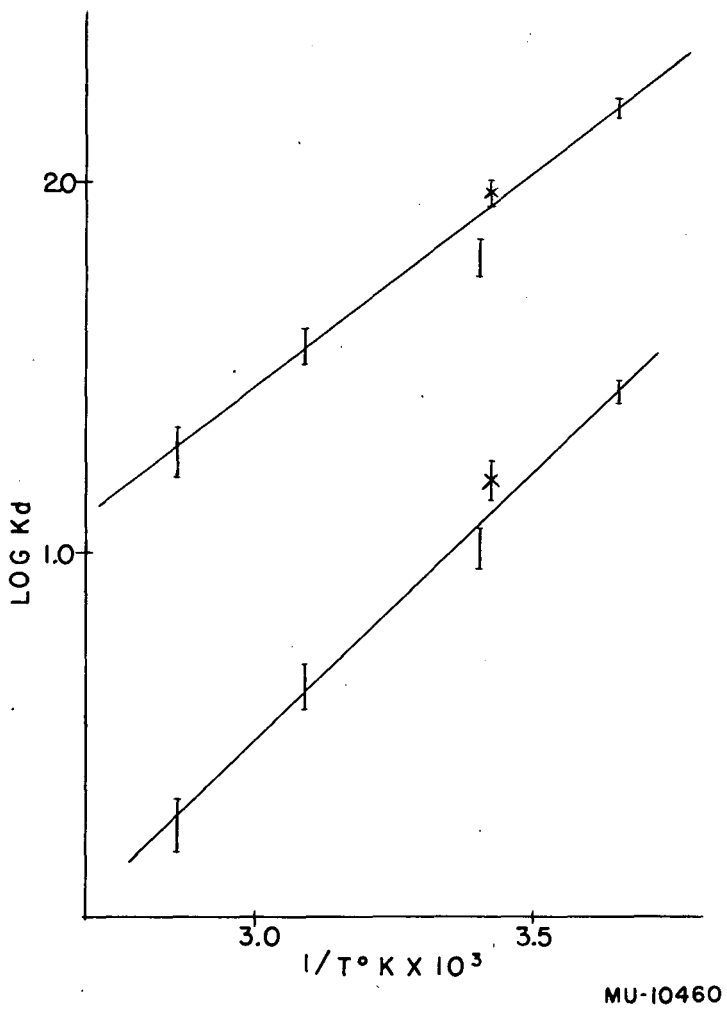

Fig. 2 Variation of logarithm of americium K_d with reciprocal of absolute temperature. Ammonium thiocyanate concentration was 3 M (upper curve) and 1 M (lower curve). "X" indicates a measurement one month after initial experiment.

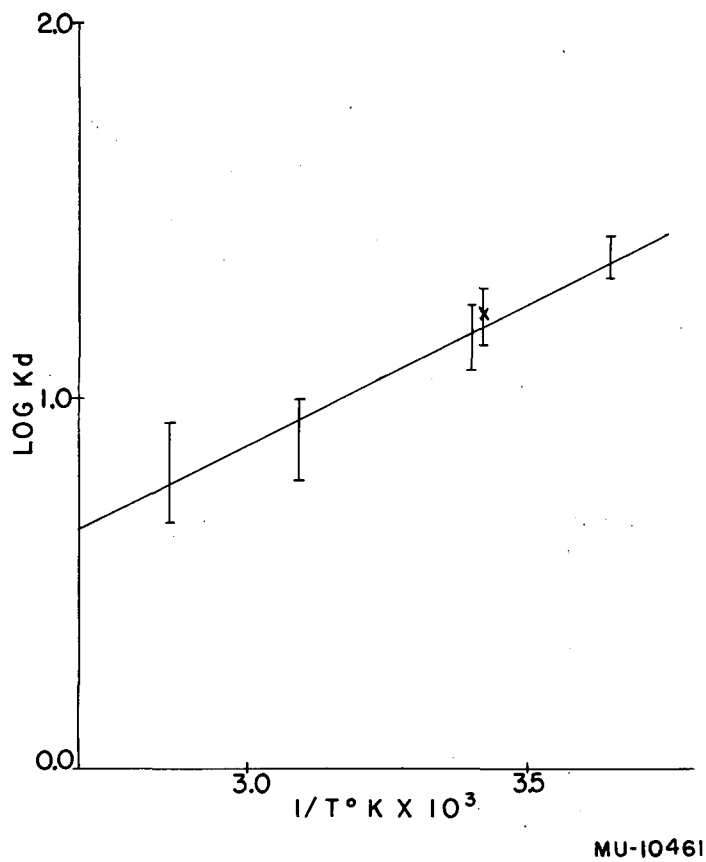

Fig. 3 Variation of logarithm of europium K_d with temperature. Ammonium thiocyanate concentration was 1 M. "X" indicates a measurement one month after initial experiment.

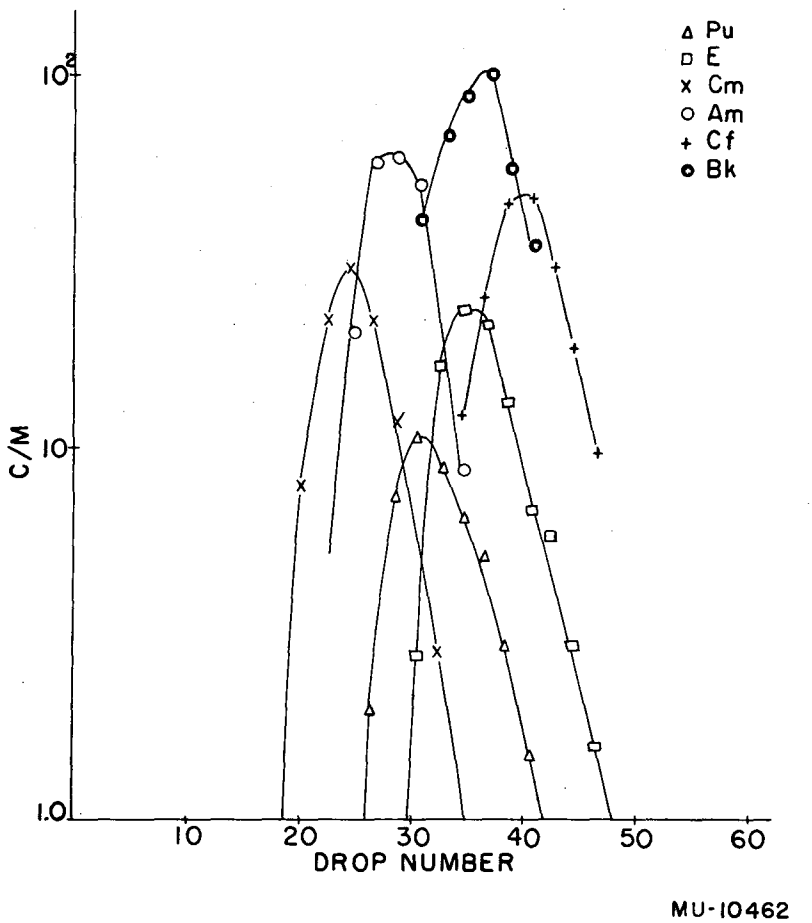

Fig. 4 Elution of actinides from Dowex-1 with 2 M ammonium thiocyanate at 87° C.

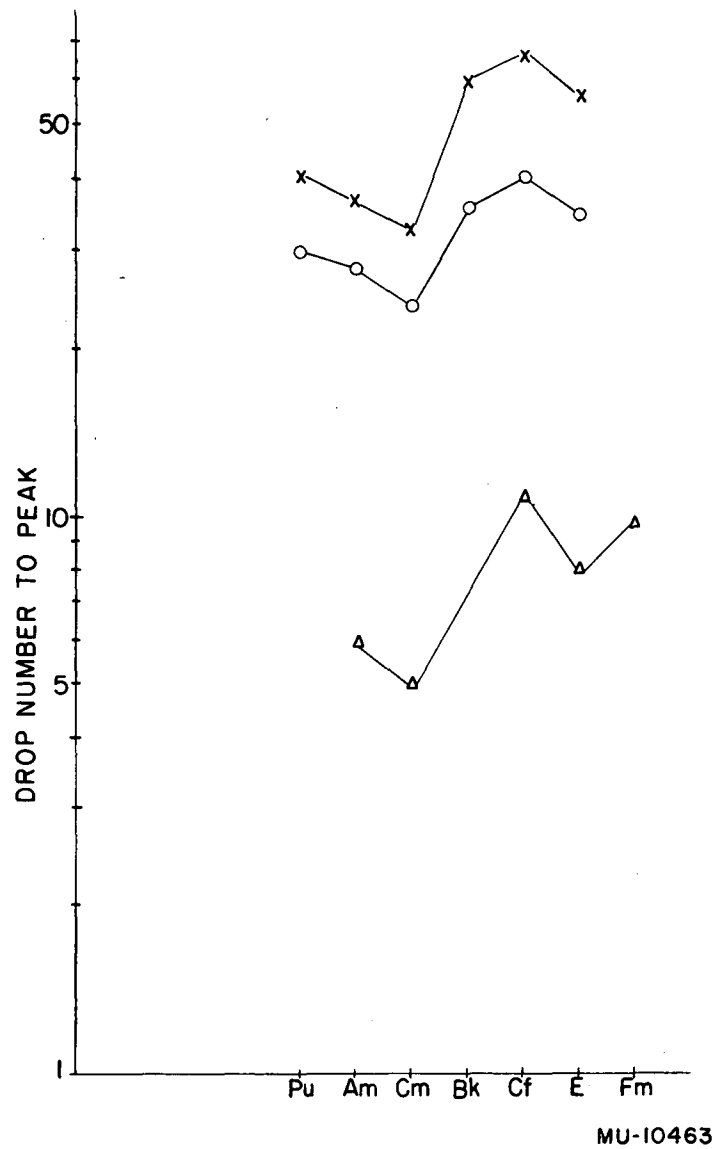

Fig. 5 Elution peak positions of actinides from Dowex-1.

X 2mm diameter x 7 cm length resin bed, 1 M NH_4SCN eluant at 33° C.

O 2 mm diameter x 6 cm length resin bed, 2 M NH_4SCN eluant at 87° C.

△ 3 mm diameter x 6 cm length resin bed, 1 M NH_4SCN eluant at 87° C.

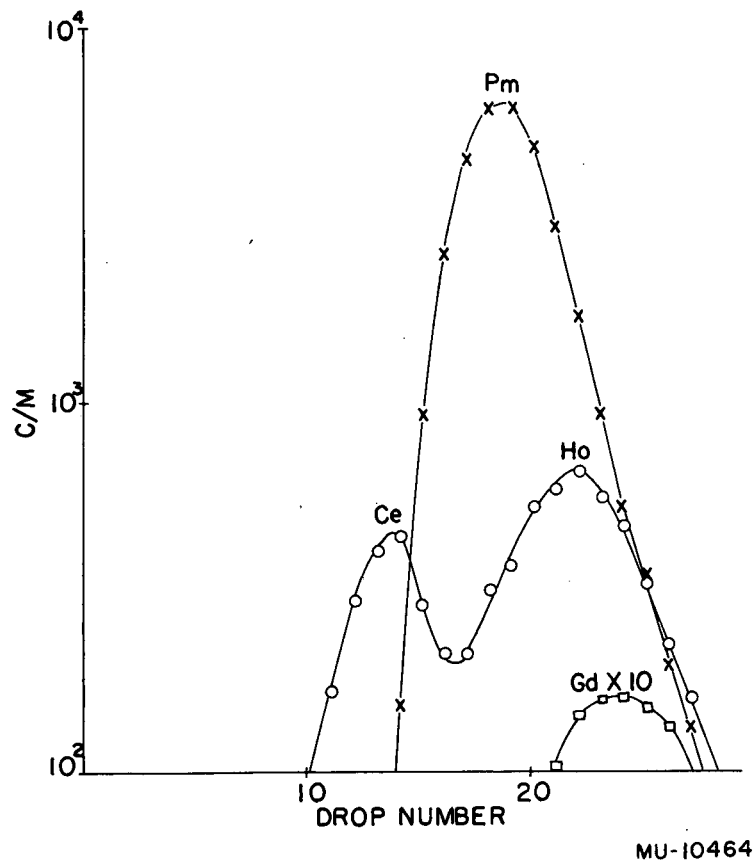

Fig. 6 Elution of several lanthanides from Dowex-1 with 2 M NH_4SCN eluant at 33° C.

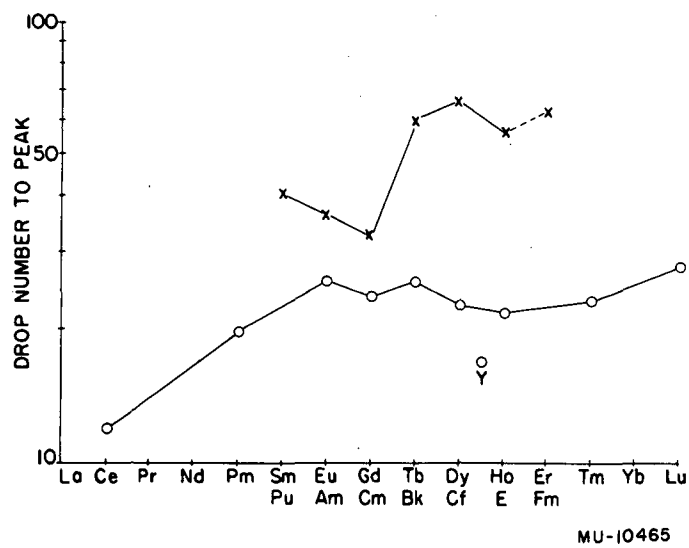

Fig. 7 Elution peak positions of lanthanides, yttrium, and actinides vs. atomic number. Actinides are plotted opposite analogous lanthanides.

X - Actinides

O - Lanthanides and yttrium

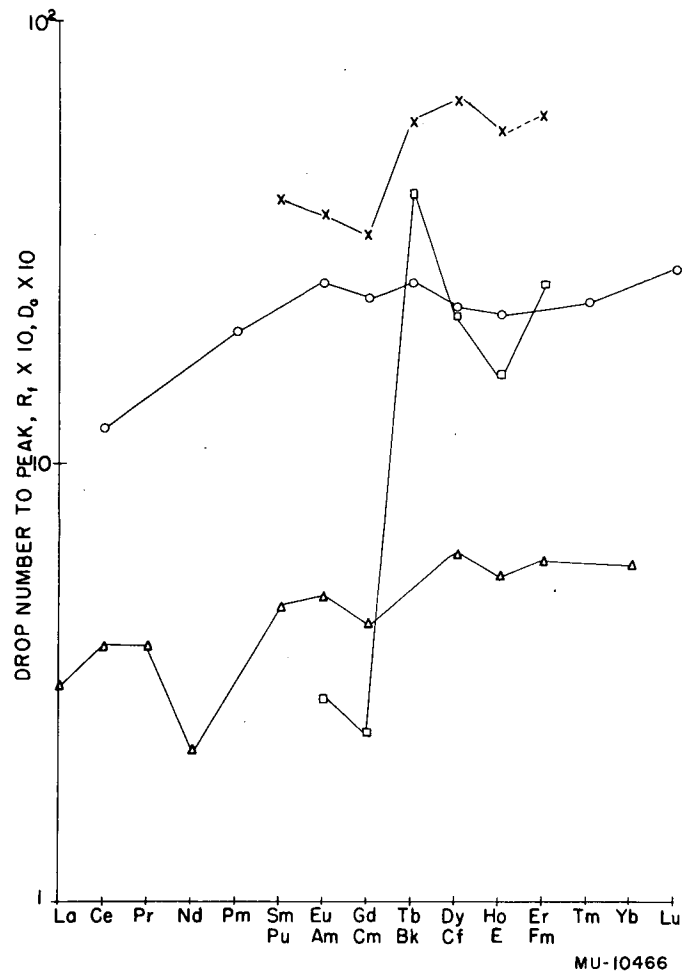

Fig. 8 Complex formation of actinides and lanthanides as a function of atomic number.

X - Actinide elution peak drop number from Dowex-1 with ammonium thiocyanate eluant.

O - Lanthanide elution peak drop number from Dowex-1 with ammonium thiocyanate eluant.

□ - D_a for actinides from reference 18.

Δ - Rf for lanthanides from reference 19.

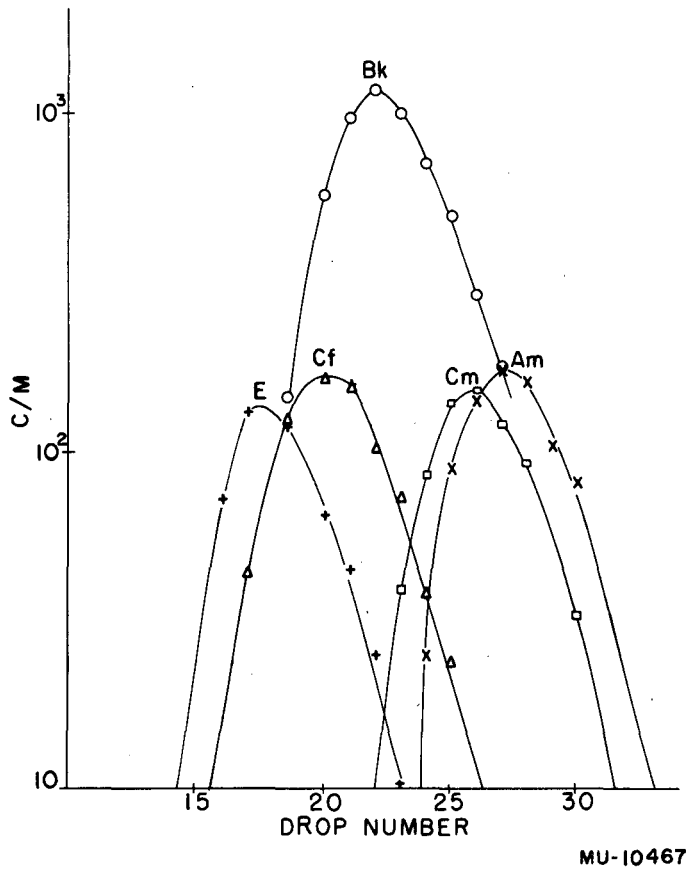

Fig. 9 Elution of actinides from Dowex-50. Resin bed 2 mm diameter x 5 cm length. 1.8 M ammonium thiocyanate eluant. 87° C.

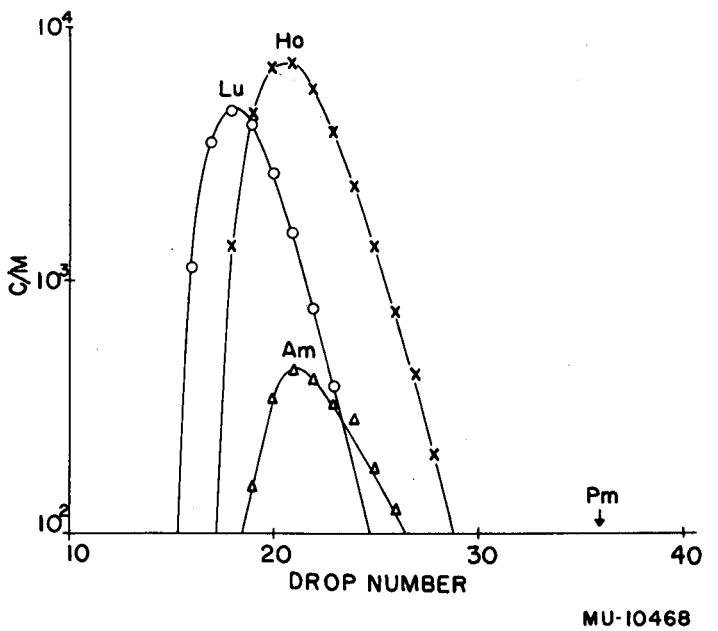

Fig. 10 Elution of lutetium, holmium, promethium, and americium from Dowex-50. Resin bed 2 mm diameter x 5 cm length. 2.0 M ammonium thiocyanate eluant. 87°C.

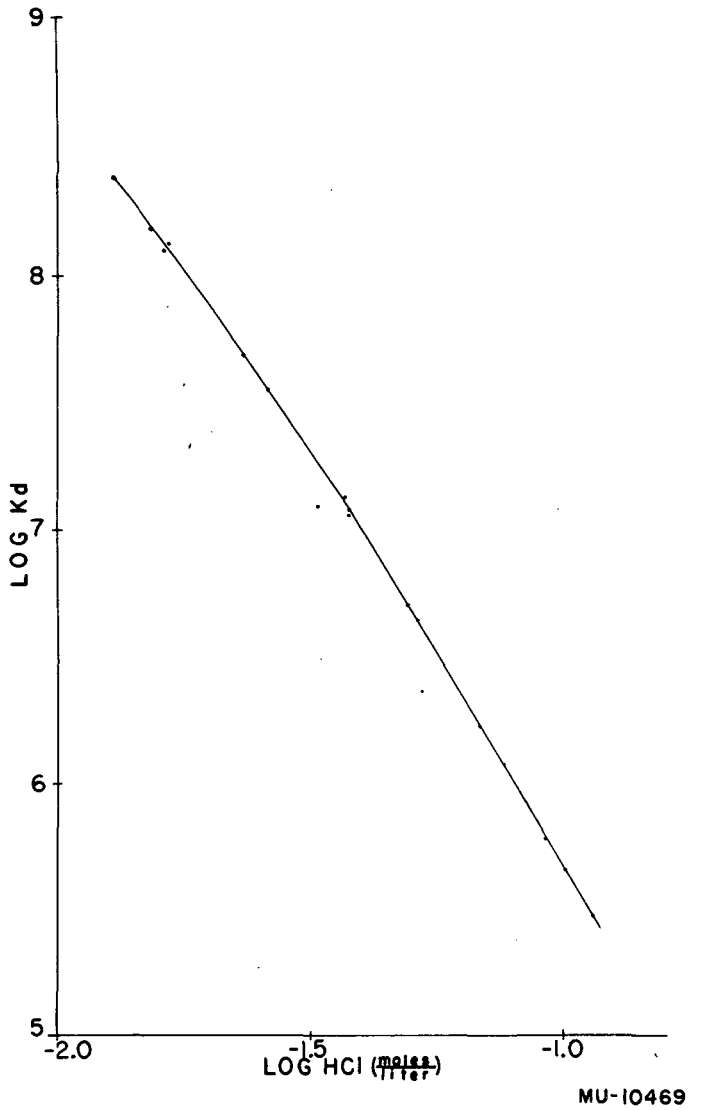

Fig. 11 Variation of logarithm of K_d for cerous ion with logarithm of hydrochloric acid concentration, 25°C.

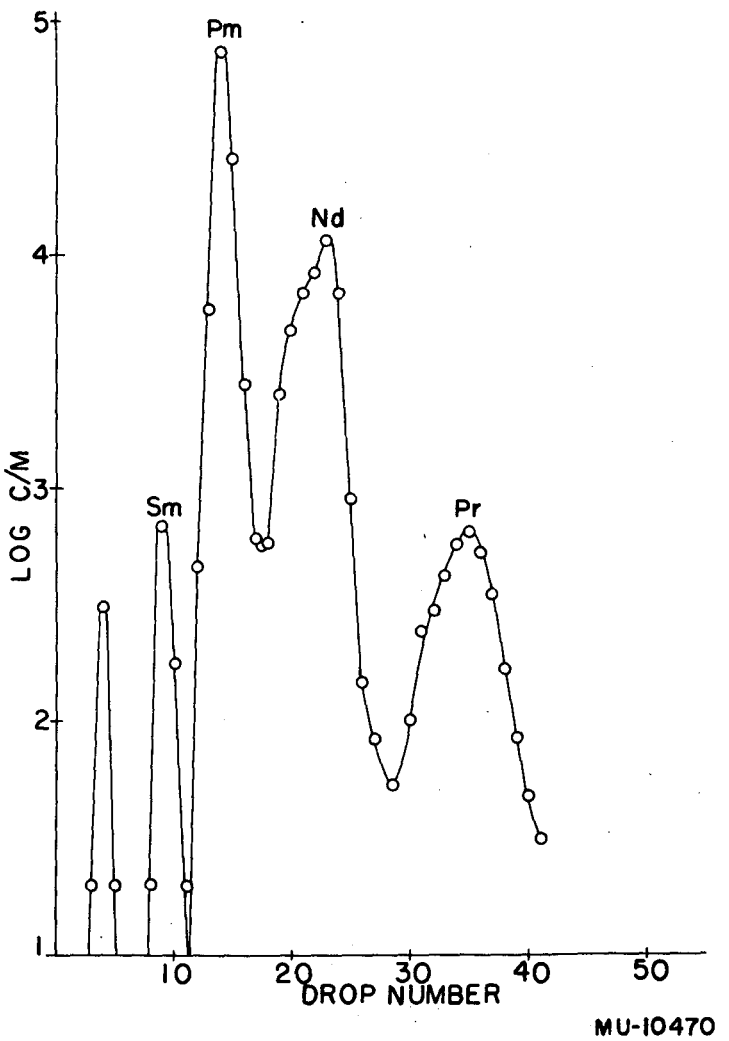

Fig. 12 Separation of neodymium after neutron irradiation. Dowex-50 resin, ammonium alpha-hydroxy isobutyrate eluant at 87°C.

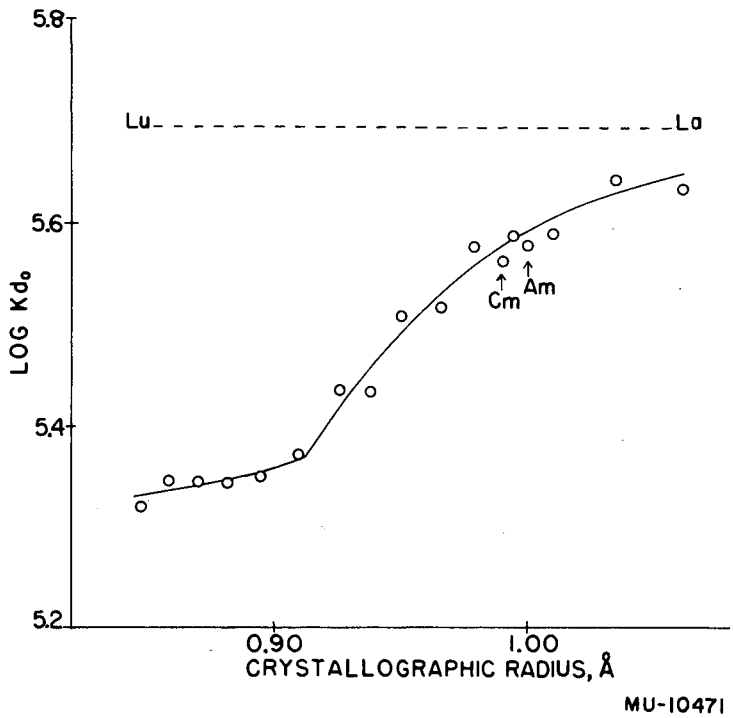

Fig. 13 Logarithm of K_{d_0} vs. the crystallographic radius for lanthanides, americium, and curium.

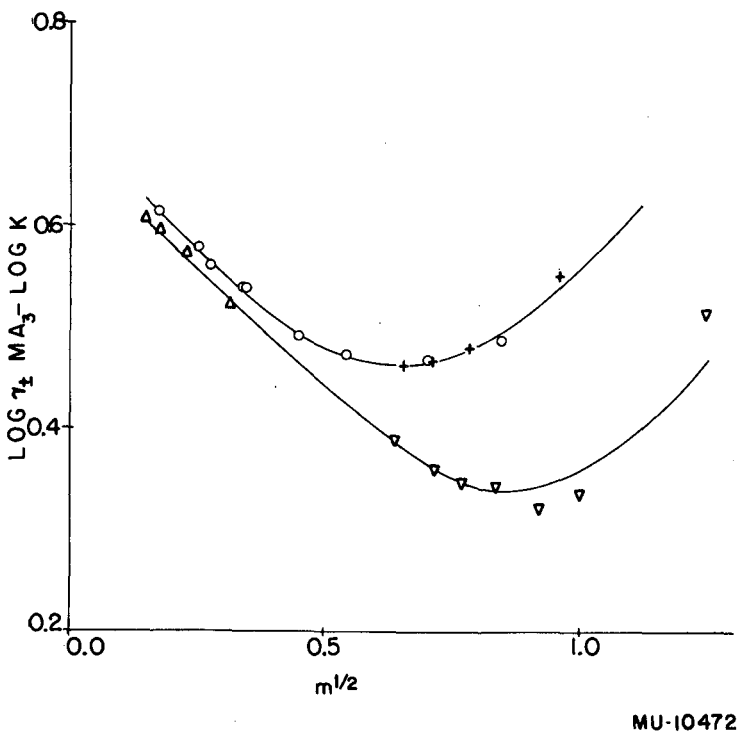

Fig. 14 Logarithm of relative activity coefficients versus square root of acid molality.

O - $M(ClO_4)_3$

+ - $Ce(ClO_4)_3$ from reference 20.

△ - $CeCl_3$

▽ - $CeCl_3$ from reference 20.