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ION-EXCHANGE BEHAVIOR AND DISSOCIATION CONSTANTS OF AMERICIUM, CURIUM, AND CALIFORNIUM COMPLEXES WITH ETHYLENEDIAMINETETRAACETIC ACID

J. Fuger

May, 1957

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J. Fuger*

ABSTRACT

Separation factors between californium, curium, and americium on ion-exchange resin Dowex-50 X-12, in ammonium form, have been calculated from static equilibrations between pH 2 and pH 3.3, in presence of EDTA 10^{-3} M. They are found to be 2.04 ± 0.05 between americium and curium and 5.5 ± 0.1 between curium and californium.

These results can be compared favorably with "column separation factors" obtained with the best known eluting agent for actinides: alpha-hydroxy-isobutyric acid, for which corresponding factors are 1.4 and 5.0 respectively.

In our experiments only 1:1 complexes are formed, and the dissociation constants are found to be equal to:

californium $= 10^{-19.09 \pm 0.2}$,
curium $= 10^{-18.45 \pm 0.1}$,
americium $= 10^{-18.16 \pm 0.1}$.

Preliminary column experiments show that this complexing agent will be quite useful for separating actinide elements.

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INTRODUCTION

Some attention has been paid already, as we know, to the complexes of actinide elements with ethylenediaminetetraacetic acid (EDTA). Cabell[1] has studied potentiometrically the titration of UO_2^{++} and Th^{+4} ions with EDTA. R. A. Glass,[2] in a thesis work, reports an unsuccessful attempt to separate americium and curium on an ion-exchange column with EDTA. Schwarzenbach[3] has determined polarographically the stability constant of EDTA with Th^{+4}. Milner and Woodhead[4] point out a volumetric determination of Pu^{+3} with EDTA. By ion-exchange method, the stability constant of Pu^{3+}, Pu^{+4}, and PuO_2^{++} complexes have been measured by Foreman and Smith.[5] These authors also made potentiometric titrations and absorption spectra measurements of the plutonium complexes in the different valency states.

In the present work, we have tried to evaluate the usefulness of EDTA as a complexing agent for separating trivalent actinide elements on an ion-exchange column, and to determine the dissociation constants of Am^{+3}, Cm^{+3}, and Cf^{+3} complexes.

For static experiments, we can define the distribution, at equilibrium, of an ion between an ion-exchange resin and the solution, by the ratio

$$K_d = \frac{\text{total amount of ion on the resin}}{\text{total amount of ion in solution}} \times \frac{\text{ml of solution}}{\text{g of dry resin}} = \frac{[\text{ion}]_R}{[\text{ion}]_S}, \quad (1)$$

without making any assumption as to the nature of the ionic species in the resin or in solution. With the radioactive ions, K_d will be expressed as

$$K_d = \frac{\text{c/m (total)} - \text{c/m (solution)}}{\text{c/m (solution)}} \times \frac{\text{ml of solution}}{\text{gr of dry resin}}, \quad (1a)$$

where c/m (total) is the total activity introduced in solution and c/m (solution), activity remaining in solution after equilibrium has been reached.

As usual, we call "separation factor α" between two ions A and B the ratio K_d^A/K_d^B.

This K_d expression (1) can easily be related to column separation experiments,[6] for which it can be defined by:

$$K_d = \left(\frac{V_M}{V_L} - 1\right) \frac{V_L}{m}, \tag{2}$$

where V_L is the free column volume, V_M is the volume of eluate corresponding to the maximum of the peak without subtracting the first free column volume, and m is the weight (in grams) of dry resin on the column.

By formula (2) we can see that the separation factor α is directly related to the separation which can be hoped for in a column experiment.

EDTA is a tetrabasic acid - H_4Y - , of which the four apparent dissociation constants are

$$\frac{[H^+]\ [H_3Y^-]}{[H_4\ Y]} = K_1, \tag{3}$$

$$\frac{[H^+]\ [H_2Y^{2-}]}{[H_3Y^-]} = K_2, \tag{4}$$

$$\frac{[H^+]\ [HY^{3-}]}{[H_2Y^{2-}]} = K_3, \tag{5}$$

$$\frac{[H^+]\ [Y^{4-}]}{[H\ Y^{3-}]} = K_4, \tag{6}$$

where, as usual, square brackets represent molar concentrations.

In the case of this ligand we can suppose that the trivalent actinide complexes have the formula MeY^-. This assumption is made by analogy with lanthanide elements for which such complexes are well known.[3,7,8] Moreover, Foreman and Smith[5] have demonstrated that the complex formed with Pu^{+3} is $Pu\ Y^-$ in analogous conditions. The equilibrium involving this complex formation is

$$Me\ Y^- \rightleftharpoons Me^{+3} + Y^{-4} \qquad \frac{[Me^{+3}]\ [Y^{-4}]}{[Me\ Y^-]} = \mathcal{K}_c, \tag{7}$$

and $\mathcal{K}_c$ is called the dissociation constant of the complex. Such a negative complex will not absorb on a cation-exchange resin, like Dowex-50, whereas Me^{3+} ion will do so.

If we call $[H_4Y]_t$ the total concentration of EDTA in solution, we can write:

$$[H_4Y]_t = [Y^{4-}] + [H\,Y^{3-}] + [H_2Y^{2-}] + [H_3Y^-] + [H_4Y] + [MeY^-]. \quad (8)$$

In the case of tracers or relatively small quantities, $[MeY^-]$ is negligible. Introducing (4), (5), (6), and (7) into (8), we obtain:

$$[H_4Y]_t = [Y^{4-}].\,\theta, \quad (9)$$

where

$$\theta = 1 + \frac{[H^+]}{K_4} + \frac{[H^+]^2}{K_4K_3} + \frac{[H^+]^3}{K_4K_3K_2} + \frac{[H^+]^4}{K_4K_3K_2K_1}. \quad (10)$$

Considering K_d expression in the particular case of EDTA complexes, we have:

$$\frac{[Me^{+3}]_R}{[Me^{+3}]_S\,[MeY^-]} = \frac{[Me^{+3}]_R}{[Me^{+3}]_S} \cdot \frac{1}{1 + \frac{[MeY^-]}{[Me^{+3}]_S}} = K_d^o \cdot \frac{1}{1 + \frac{[MeY^-]}{[Me^{3+}]_S}}, \quad (11)$$

where K_d^o is the distribution coefficient of Me^{3+} ion in absence of a complexing agent, all other conditions remaining the same.

Combining (7), (9), and (11), K_d becomes:

$$K_d = K_d^o \cdot \frac{1}{1 + \frac{[H_4Y]_t}{\theta \cdot \mathcal{K}_c}}. \quad (12)$$

Therefore, if we can determine K_d and K_d^o in the same range of pH and the same conditions, and provided we know θ from dissociation constants of EDTA, we are able to calculate, for each plot of K_d, the dissociation constant $\mathcal{K}_c$ of the complex MeY^-.

EXPERIMENTAL

Apparatus and reagents:

All these experiments were made at 25° ± 0.02, by stirring a well-known amount of resin with a solution containing a fixed concentration of EDTA and the tracer. Experiment showed that equilibrium between resin and solution was obtained in less than half an hour. Nevertheless, equilibration was usually allowed to continue overnight.

Dowex-50 X-12 resin was used in ammonium form. First, this resin was graded to settle, in acid form, at 0.75 - 1.25 cm per minute in water. Six successive gradings were made in order to eliminate coarse and, above all, very small particles, which might have given trouble in some of these experiments. Purification of the resin in ammonium form was accomplished by washing it on a column with, successively, 20 free column volumes of 1 M HCl, 6 M HCl (HCl prepared free from iron with HCl gas and conductivity water), conductivity water, 6 M NH_4OH, conductivity water, 2.5×10^{-2} M EDTA, at pH 4.2. This procedure is quite effective in removing common contaminants such as aluminum, iron, copper, etc. A spectrographic arc analysis of 9 mg of purified resin gave the following results (Plate No. 1314):

Iron	: < 0.01 μg	Calcium	: < 0.01 μg
Copper	: < 0.01 μg	Sodium	: < 1 μg
Aluminum	: < 0.1 μg	Silicon	: 0.01 μg
Magnesium	: 0.01 μg	Nickel	: < 0.01 μg

(< indicates below the limit of detection)

The resin was dried overnight at 105-110°C and kept in a vacuum desiccator. Weighing of the resin was done in closed glass weighing bottles in order to prevent absorption of moisture.

Samples were equilibrated in ground-glass-stoppered 12-ml cones (sealed with Dow Chemical silicone grease), attached to a rotating wheel immersed in the thermostatic bath. The pH meter used was the Beckman Model G, standardized at pH 4 with commercial Beckman Buffer and with a specially prepared potassium acid phthalate buffer. Special care was taken in pH measurements because pH is the most important factor in K_d values. The pH meter was standardized several times during each series of measurements. Measurements were taken of each individual solution, after equilibrium had been reached, with an accuracy of 0.01 pH unit.

The EDTA used was obtained in C.P. grade from Bersworth Chemical Co., Framingham, Mass. No impurities were detected in a 1-mg sample by an arc and spark spectrographic analysis. All other reagents were of analytical grade. Glassware was boiled with 6N HNO_3, then washed with conductivity water. Alpha counting was done in the usual two pi-alpha chambers with a proportional counter. Except for equilibration at 25°C, all the manipulations, including pH measurements, with activities higher than 10^5 - 10^6 c/m were made in a Berkeley box.

Solutions and tracers

Solutions to be equilibrated were made exactly 10^{-3} M in EDTA by adding to the solid a known amount of a standardized NH_4OH solution (to obtain pH 4.50), and were then made exactly 0.1 M in NH_4^+ by adding NH_4ClO_4. The tracer was added in several drops of 0.05 M $HClO_4$ solution. Then, for each sample, the pH was adjusted to the desired value with small quantities of $HClO_4$. The solutions used in K_d^o measurements were 0.1 M in NH_4ClO_4. The pH was adjusted in the same way. For these equilibrations, very small quantities of resin were used: 2 to 10 mg weighed to ± 0.005 μg in small closed containers with an Ainsworth Model V.M. Balance.

The tracers used were Am^{241} (α: 5.48 Mev-- $t_{1/2}$: 461 years) Cm^{244} + 0.2% by mass Cm^{242} (respectively, α: 5.80 and 6.11 Mev-- $t_{1/2}$: 19 years and 162 days); and Cf^{252}(α: 6.112 Mev-- $t_{1/2}$ α: 2.2 years; spontaneous fission: 66 years). Americium and curium tracers used were pure both chemically and radiochemically.

Californium was recovered from a previous electroplating on a stainless steel plate by dissolving the surface of the plate in HCl. Fe^{3+} was eliminated by passing the active solution in 6 M HCl through a Dowex A-1 X-10 anion resin in chloride form.[9] A further purification and concentration was obtained by absorbing the californium (in 0.05 M HCl solution) on Dowex-50 X-4 and eluting it with 6 M HCl.[10] Ninety percent of the californium was concentrated in four drops of eluate, and spectrographic analysis (plates No. 1298, 1302, and 1304) showed that it was nicely separated from all the elements (iron traces, chromium, nickel, manganese) originally contained in the stainless steel plate and from the lanthanum present (50 μg) in the electroplated californium. The total californium activity, 8.10^5 dpm, used for this work contained less than 4 micrograms of other cations. A pulse analysis showed that the californium was pure from other alpha activity.

Mounting the plates, and sample counting

Unless otherwise indicated, activity measurements were made at equilibrium from the solution phase. After a short time of settling, aliquots of the solutions were taken by means of a transfer pipette with a tight glass wool plug in the tip (in order to filter small particles of resin from the aliquot); then the tip was broken off and the aliquot transferred in a small

container; occasionally two aliquots were picked up with two different pipettes to check the absence of fluctations which would indicate that some small quantities of resin are passing through the plug. In order to perform this pipetting it was necessary to connect the pipette to a vacuum line.

Samples of 50λ (or 100 λ for californium) of the aliquots were mounted on platinum plates and dried slowly under a heat lamp. Continued heating resulted in vaporization of NH_4ClO_4. The plates were not flamed since this sometimes led to losses of about 5%. At least two plates were prepared and counted for the same equilibration (occasionally from two different aliquots).

By means of long counting times the statistical error was kept below 1% except for the lowest counting rates. The fluctuation between two different plates from the same equilibration usually was in the range of the statistical error (calculated as σ); when this was not the case, new plates were mounted.

RESULTS AND DISCUSSION

K_d determinations

At 10^{-3}M EDTA concentration, the suitable range for K_d measurements was found between pH 2 and pH 3.3. Results of measurements are shown in Table I, and Curve 1 gives a graph of K_d vs pH.

In Table I the values in column "Total Activity" are the amounts (in c/m) used for each equilibration. These amounts are averages of 6 or more assays.

The two lowest points on the plots of the americium and curium K_d graphs were obtained by measuring the activity absorbed in the resin. This should be more accurate when the activity left in solution is very close to the total activity. The resin was separated from the solution by centrifugation through a platinum Gooch crucible. The resin was then equilibrated with an EDTA solution of pH higher than 4, and the activity, which at this pH can be assumed to be quantitatively in solution, was measured by the usual techniques. Table I, for these two measurements, gives thus the difference between total activity and activity found in the resin. Small confidence can be given to the accuracy of these two points on the K_d plots, because of the possibility that some solution was left on the surface of the resin. Nevertheless, we can assume they are accurate to ± 10%.

Table I

Element	Weight of Resin (grams)	pH at Equilibrium	Total Activity (c/m per 50λ)	Activity in Sol. at Equilibrium (c/m per 50λ)	K_d	Vol. of Solution (ml)
Am	0.09255	2.06	10,283 ± 16	132 ± 3	8190	10
	0.13566	2.16	"	181 ± 1	4100	"
	0.14270	2.22	"	265 ± 1	2640	"
	0.16900	2.40	"	752 ± 4	750	"
	0.20036	2.68	"	2,887 ± 12	128	"
	0.24042	2.72	"	3,262 ± 13	89.5	"
	0.22508	2.83	"	5,420 ± 17	39.8	"
	0.30130	3.02	"	7,624 ± 18	11.6	"
	0.35311	3.18	"	8,458* ± 35	6.1	"
Cm	0.16834	2.19	3,422 ± 10	142 ± 4	1370	10
	0.22060	2.22	"	108 ± 2	1480	"
	0.19033	2.72	"	1,834 ± 9	45.4	"
	0.06979	2.00	5,736 ± 20	173 ± 2	4620	"
	0.19686	2.11	"	103 ± 4	2780	"
	0.20423	2.38	"	583 ± 10	430	"
	0.26923	2.62	"	1,999 ± 7	69.4	"
	0.23110	2.84	"	4,004 ± 14	18.7	"
	0.39152	2.94	"	4,230 ± 9	9.09	"
	0.24197	3.00	"	4,870 ± 16	7.51	"
	0.26752	3.01	"	4,826 ± 15	7.04	"
	0.50880	3.26	"	5,000* ± 25	2.89	"
			100 λ	100 λ		
Cf	0.02890	2.03	408 ± 1	112.6 ± 1	909	10
	0.04600	2.16	"	145.3 ± 1	394	"
	0.06801	2.24	"	177.3 ± 0.5	192	"
	0.06857	2.42	"	240.0 ± 2	51.0	5
	0.18651	2.53	"	286.1 ± 1	22.9	10
	0.09196	2.80	"	380.2 ± 1	4.00	5

*Measured from activity in the resin phase; see text.

The separation factors calculated from Table I and Curve 1 are:

$$\alpha_1 = \frac{K_d^{Am}}{K_d^{Cm}} = 2.04 \pm 0.05,$$

$$\alpha_2 = \frac{K_d^{Cm}}{K_d^{Cf}} = 5.5 \pm 0.1.$$

These values can be favorably compared with those obtained by column method (Dowex-50 X-12) with alpha-hydroxyisobutyric acid:[11]

$$\alpha_1 = 1.4,$$

$$\alpha_2 = 5.0.$$

K_d^o determinations

K_d^o determination results are shown in Table II, and reproduced in Curve 2. Some fluctuations are observed in the plots, the largest deviation being about 5% from the curve.

Because of high K_d^o values, the quantities of active isotopes used for these equilibrations were rather high; for americium experiments, they are on the order of 2.8 μg americium/10ml. It is easy to calculate that this concentration of americium can saturate less than 0.5% of the smallest quantity of resin used (2 mg).

Stability constants

Schwarzenbach and Ackermann [12] and, more recently, Cabell[1] have determined, by potentiometric titrations, the dissociation constants of EDTA; both groups made their experiments under the same conditions: 0.1 M KCl - 20°C - EDTA about 10^{-3}M. Carini and Martell,[13] in a study of EDTA dissociation constants as a function of ionic strength (KCl), found, for the product K_1K_2 and for K_3 in 0.1 M KCl, values in very good agreement with those of Cabell.

The differences between EDTA values found by Schwarzenbach (as shown in Table III) and those given by Cabell lead to a discrepancy of 0.4 ± 0.05 p $\mathcal{K}_c$ unit in the absolute values calculated for the stability constant of actinide complexes, but do not affect the relative values of these dissociation constants.

Table II

Element	Weight of resin (mg ± 5 μg)	pH	Total Activity (c/m per 50λ)	Act. in Sol. at equilibrium (c/m per 50λ)	$K_d^o \times 10^{-5}$	ml
Am	4.935	1.74	50,337 ± 50	653 ± 4	1.54	10
	5.460	2.02	"	451 ± 4	2.02	"
	7.375	2.17	"	292 ± 3	2.32	"
	2.015	2.20	"	1,076 ± 5	2.28	"
	5.450	2.40	"	354 ± 6	2.59	"
	5.530	2.56	"	319 ± 3	2.85	"
	4.730	2.80	"	361 ± 3	2.92	"
	2.640	3.23	"	581 ± 4 {637 ± 6	3.24 2.95}	"
Cm	4.915	1.77	47,580 ± 50	701 ± 3	1.36	10
	9.705	1.96	"	294 ± 2	1.65	"
	7.195	2.12	"	352 ± 3	1.85	"
	8.295	2.21	"	259 ± 2	2.20	"
	6.060	2.41	"	345 ± 3	2.26	"
	3.595	2.48	"	578 ± 4	2.26	"
	5.410	2.60	"	332 ± 3	2.64	"
	6.295	2.83	"	281 ± 1	2.67	"
	2.310	3.32	"	706 ± 3	2.87	"

Table III

Acid Dissociation Constants of EDTA – 20°C – 0.1 M KCl

	Cabell	Schwarzenbach and Ackermann
pK_1	2.24_1	1.99_6
pK_2	2.95_1	2.67_2
pK_3	6.24_0	6.16_1
pK_4	10.31_6	10.26_2

We have tried to decide, with our experimental data, which of the EDTA dissociation-constant determinations seemed to be the more accurate.

In the range of our K_d measurements, formula (12) can be simplified:

$$\frac{K_d}{K_d^o} = \frac{\theta \cdot \mathcal{K}_c}{[H_4Y]_t} \quad (13)$$

Thus, a plot of $\frac{K_d}{K_d^o}$ vs. pH must have the same slope as a plot of θ vs pH.

Comparing this $\frac{K_d}{K_d^o}$ slope with the θ function slope obtained respectively from Cabell's and Schwarzenbach-Ackermann's measurements, we observed perfect agreement with Cabell results, whereas Schwarzenbach-Ackermann's results gave a θ slope somewhat different. Consequently, as we can see in Table IV, Cabell's results led to a better agreement between the dissociation constants calculated from each point of the K_d plot. We should point out that the coincidence between the θ slope and $\frac{K_d}{K_d^o}$ slope as a function of pH is the best proof that our assumption as to the 1:1 form (MeY^-) of the complex was correct.

While the quoted dissociation constants for EDTA were determined at 20°C, our measurements were made at 25°C. Nevertheless, from Martell and co-workers' data on the influence of temperature on the third and fourth dissociation constants of EDTA,[14] on dissociation constants of the analogue nitrilo-triacetic acid,[15] and other aminoacid analogues,[16] it can be seen that the change in θ function of EDTA between 20°C and 25°C will affect the actinide dissociation constants of less than 0.05 p$\mathcal{K}_c$ unit.

The reason why we have chosen NH_4ClO_4 to obtain μ:0.1 rather than KCl, is that ClO_4^- ions complex actinide ions little if at all, while Cl^- ions do.[17,18] Moreover, NH_4ClO_4 can be easily destroyed by heating without leaving a residue, and this facilitates the radioactivity measurements.

K_d^o in Table IV is taken from Curve 2. We had no opportunity to determine K_d^o for californium; we calculated these K_d^o values, assuming that the difference between $K_d^{o\ Cm}$ and $K_d^{o\ Cf}$ is twice the difference $K_d^{o\ Am} - K_d^{o\ Cm}$; in other words:

Table IV

Element	pH of K_d plot	K_d Value	$K_d^o \times 10^{-5}$ from Curve 2	Actinide Stability Constants: From Cabell's θ Values: $\theta \times 10^{-10}$	p$\mathcal{K}_c$	From Schwarzenbach's θ Values: $\theta \times 10^{-10}$	p$\mathcal{K}_c$
Am	2.06	8,190	2.11	5,700	18.16	1,800	17.67
	2.16	4,100	2.25	2,550	18.15	820	17.65
	2.22	2,640	2.35	1,610	18.15	540	17.68
	2.40	750	2.59	426	18.17	150	17.71
	2.68	128	2.88	55.5	18.11	24.5	17.74
	2.72	89.5	2.91	44	18.14	19.4	17.79
	2.83	39.8	2.97	20.3	18.18	9.8	17.87
	3.02	11.6	3.05	6.4	18.23	3.5	17.96
				Average	18.16	Average	17.76
Cm	2.00	4,620	1.75	9,175	18.54	2,720	18.01
	2.11	2,780	1.93	3,700	18.41	1,200	17.93
	2.19	1,370	2.05	2,050	18.48	660	18.00
	2.22	1,480	2.09	1,610	18.36	540	17.88
	2.38	430	2.31	477	18.41	175	18.00
	2.62	69.4	2.57	84	18.49	35.5	18.12
	2.72	45.4	2.64	44.0	18.41	19.4	18.05
	2.84	18.7	2.73	19.8	18.46	9.5	18.14
	2.94	9.09	2.76	10.4	18.50	5.5	18.22
	3.00	7.51	2.81	7.4	18.44	4.04	18.18
	3.01	7.04	2.82	6.7	18.43	3.75	18.18
				Average	18.45	Average	18.06
			K_d^o calculated				
Cf	2.03	909	1.38	7,300	19.14	2,250	18.53
	2.16	394	1.48	2,550	18.98	820	18.49
	2.24	192	1.58	1,380	19.06	470	18.59
	2.42	51.0	1.84	360	19.00	134	18.68
	2.53	22.9	1.98	157	19.13	65	18.75
	2.80	4.00	2.21	25.4	19.15	12.4	18.84
				Average	19.09	Average	18.65

$$K_d^{o\ Cf} \simeq K_d^{o\ Cm} - 2\,(K_d^{o\ Am} - K_d^{o\ Cm}). \qquad (14)$$

As shown by Surls,[19] using Dowex-50 X-4 resin, K_d values for the lanthanide elements, and americium and curium, depend essentially on the ionic radii. This interpolation allows us to estimate $\mathcal{K}_c$ for californium to within $\pm 0.2\,p\mathcal{K}_c$ unit. And for americium and curium dissociation constants we estimate our error at $\pm 0.1\ p\mathcal{K}_c$ unit.

Foreman and Smith[5] give for the dissociation constant of Pu^{+3} complex: $p\mathcal{K}_c = 18,12 \pm 0.1$, calculated from Cabell's EDTA dissociation constants. In comparison with our $p\mathcal{K}_c$ value for Am^{+3}, that for Pu^{+3} is somewhat higher than might be expected. Nevertheless, we think that the agreement is satisfying considering the fact that these authors made their determinations in 0.1 M KCl at 20°C, while ours were made in 0.1 M NH_4ClO_4 at 25°C.

Column experiments

Only three experiments have been done, but all show that californium, curium, and americium behave in the same way as do heavier lanthanide elements and that the exchange reaction between complex and resin phase is fast enough so that EDTA can be used quite effectively for column separation of actinides.

A check experiment reproducing the conditions chosen by R. A. Glass,[2] 2.5×10^{-2} M EDTA – pH 3.2 elution at 80°C – column 17 cm x 2 mm, showed that these conditions were not adequate, because curium and americium were eluted in one peak with the first free column volume. Nevertheless, in this experiment a pulse-height analysis of the peak showed a noticeable separation, curium being concentrated in the ascending part of the peak. With a mixture of an yttric rare earth and yttrium, for instance, we should observe, as we know,[20] the same behavior.

Another experiment with californium, curium, americium, and promethium under different operating conditions gave the elution curve shown in Figure 3. Experimental conditions are indicated below the curve. These conditions were far from ideal. The activity was poured on the column in 20λ 0.03 M $HClO_4$. Because of the poor buffering power of the eluting solution we can really assume that, in the beginning of the elution, the column was not operating at

pH equilibrium. Nevertheless, the cross contamination between the peaks is low, and a pulse-height analysis of the two drops corresponding to the maximum of curium and americium showed that they contained, respectively, curium 99%, americium 1%; and americium 98%, curium 2%.

A loading of the column with activities in 0.01 M acid or less is thus advisable. An elution at a pH somewhat lower (2.8 - 2.9) will shift back americium and curium and give a quantitative separation. At any rate, theoretical separation factors do not seem to be overestimated.

Another important fact that should be pointed out is that, with EDTA, promethium is eluted after americium, and quantitatively separated, as it can be predicted by stability constants, whereas, with α-hydroxyisobutyric acid promethium is eluted between curium and americium.[21] On the basis of stability constants, EDTA should be a useful complexing agent for separation of the heaviest actinide elements from rare earth fission products.

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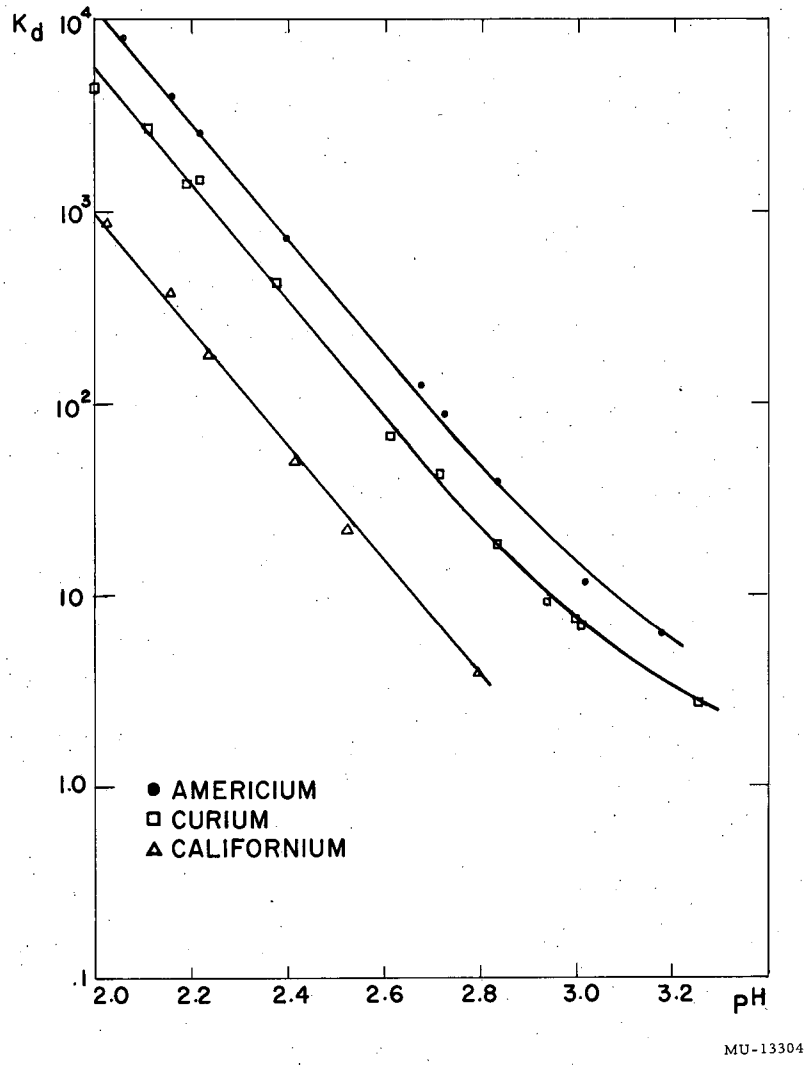

Fig. 1. K_d vs pH – 25°C.
Solution: 10^{-3} M EDTA – 0.1 M NH_4ClO_4.
Resin: Dowex-50 X-12, ammonium form.

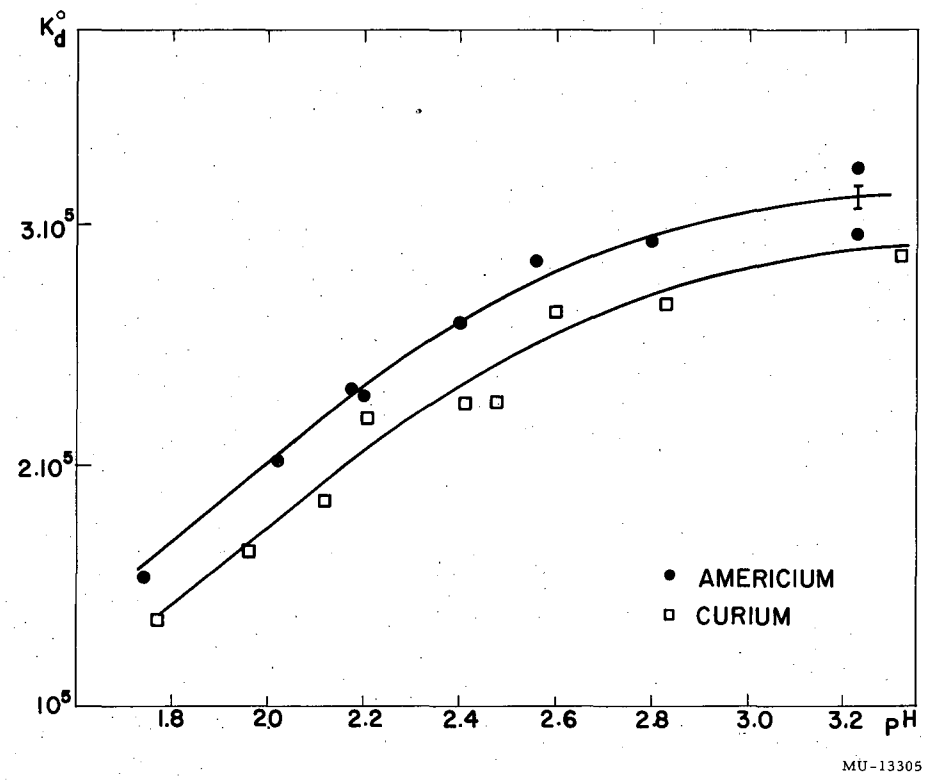

Fig. 2. K_d^o vs pH – 25°C.
Solution: 0.1 M NH_4ClO_4.
Resin: Dowex-50 X-12, ammonium form.

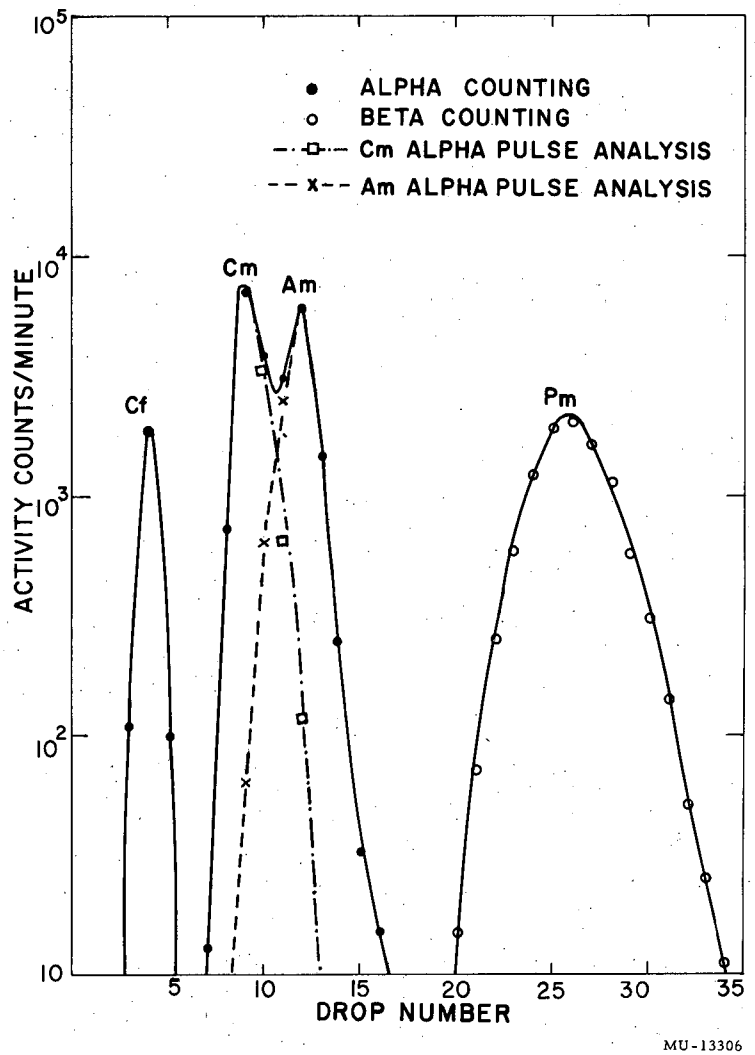

Fig. 3. Column separation of a mixture of californium, curium, americium, and promethium.

Operating conditions:

Resin bed: 5 cm x 0.2 cm, 80°C.

Dowex-50 X-12, ammonium form (rate of settling in acid form 0.75 – 1.25 cm/minute).

Eluting agent: 10^{-3} M EDTA – 0.1 M NH_4ClO_4, pH 3.00 measured at 20°C.

Flow rate: 1 drop (28λ)/4 minutes.

Activity poured on the column in 20 λ 0.03 M $HClO_4$.