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TALSPEAK: A NEW METHOD OF SEPARATING  
AMERICIUM AND CURIUM FROM THE  
LANTHANIDES BY EXTRACTION FROM AN  
AQUEOUS SOLUTION OF AN AMINOPOLYACETIC  
ACID COMPLEX WITH A MONOACIDIC  
ORGANOPHOSPHATE OR PHOSPHONATE

Boyd Weaver  
F. A. Kappelmann



**OAK RIDGE NATIONAL LABORATORY**

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CHEMICAL TECHNOLOGY DIVISION  
Chemical Development Section C

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## ABSTRACT

Talspeak is an effective new method for the separation of americium and curium from the lanthanide elements which does not involve high concentrations of any salt or acid and is resistant to the effects of irradiation. This method is being developed as a possible alternative to the Tramex process currently in use to separate trivalent actinides from lanthanides by extracting with tertiary amine chlorides from concentrated lithium chloride solutions.

Basically, the Talspeak process consists in highly preferential complexing of the trivalent actinides by an aminopolyacetic acid, so that the lanthanides and yttrium are much more strongly extracted by a monoacidic organophosphate or phosphonate. Simple carboxylic acids in the aqueous phase are helpful as buffers and solubilizers of the complexing agent. (In the absence of aminopolyacetic acids, simple carboxylic acids shift the relative extractabilities of the two groups of elements by dialkylphosphoric acids, but not enough to give an effective group separation.) Single-stage separation factors between neodymium, the least extractable lanthanide, and americium are about 50 in extractions with aromatic hydrocarbon solutions of di(2-ethylhexyl)phosphoric acid (HDEHP) from 1 M solutions of any of several carboxylic acids containing only 0.05 molar pentasodium diethylenetriaminepentaacetate ( $\text{Na}_5\text{DTPA}$ ), the most effective complexing agent tested, at pH 2.5 to 3.5. Other aminopolyacetic acids give smaller separation factors and/or are unsuitable because of solubility limitations. The presence of nitrate in the aqueous solution does not decrease the separation.

After adjustment of the lanthanide-free aqueous solution to about pH 1.5, the actinides are readily extractable with a dilute solution of

HDEHP in a suitable hydrocarbon diluent. The extracted elements may be stripped from the extractant by a dilute mineral acid.

A tentative process flowsheet that should give complete separation of americium and curium from the lanthanides includes two cycles of extraction and one of stripping. It is based on single-stage experimental data from studies of variation of extractability as a function of identity and concentration of extractant, composition of diluent and modification of aqueous phases. Americium was completely separated from europium by this process in an application of the technique of extraction chromatography, thus confirming the group separation power of the method on a multistage basis.

## 1. INTRODUCTION

Talspeak<sup>\*</sup> is a new and very effective method of separating americium and curium from the chemically similar lanthanides, which always occur as fission products in the production of the actinide elements. In a continuing search it is the first practicable alternative found to the Tramex process, in which the trivalent actinides are separated from the lanthanides by preferential extraction of the actinides with a tertiary amine from concentrated lithium chloride solutions.<sup>1,2</sup> The Tramex process is now being developed for use in purifying americium, curium, californium, and other actinides which will be produced in increasing quantities by irradiation of heavy isotopes of plutonium and the heavier actinides in a reactor with a very high neutron flux. Advantageous alternatives to the Tramex process must provide comparable group separation factors, must not require highly corrosive chemicals, and must be resistant to the effects of very high exposures to radiation. This new method shows promise of fulfilling these requirements.

Basically this new method (Fig. 1) promotes highly preferential extraction of the lanthanides with hydrocarbon solutions of monoacidic organophosphates or phosphonates by preferential complexing of the trivalent actinides in an aqueous solution with a suitable aminopolyacetic acid. The extractants which have shown most promise are di(2-ethylhexyl)-phosphoric acid (HDEHP) and 2-ethylhexyl phenylphosphonic acid (HEH[ $\phi$ P]), and the most effective aqueous complexing agent tested is diethylenetriaminepentaacetic acid (DTPA). Simple carboxylic acids are useful buffers in the aqueous solutions and increase the solubilities of the complexing agents.

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<sup>\*</sup>The name "Talspeak" is derived from Trivalent Actinide-Lanthanide Separations by Phosphorus reagent Extraction from Aqueous Complexes.

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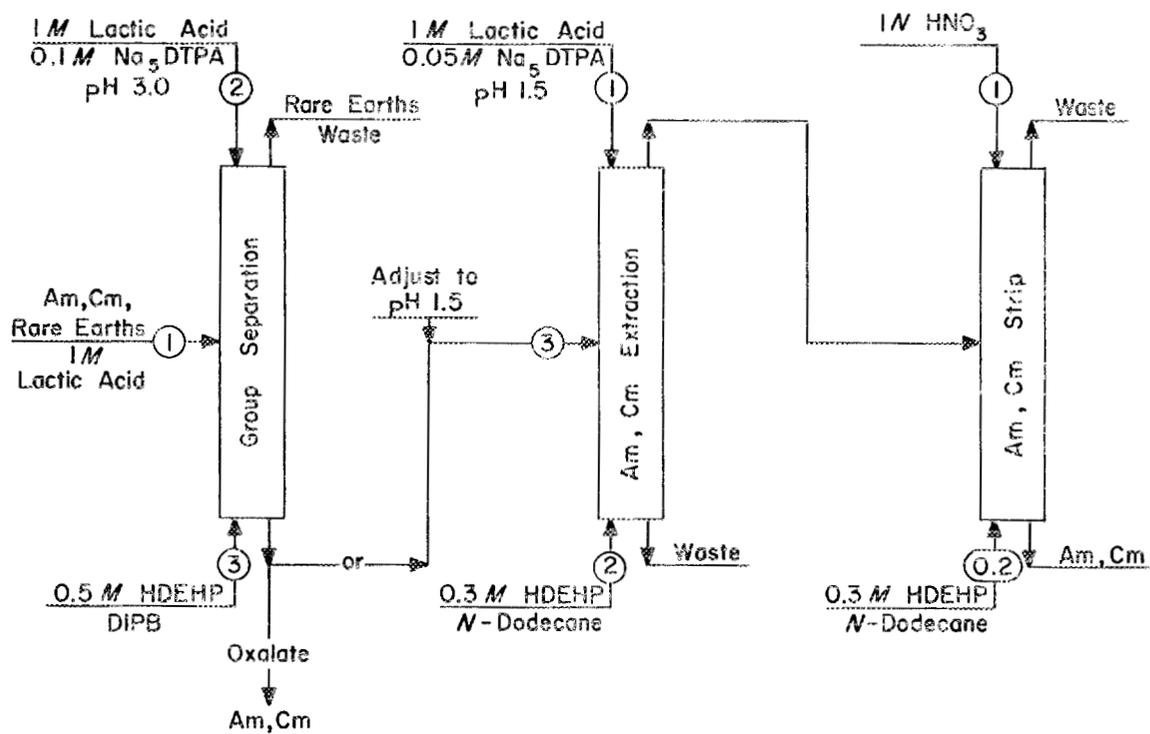


Fig. 1. Flowsheet for Purification of Americium and Curium.

After adjustment of the lanthanide-free aqueous solution to pH 1.5, americium and curium are recovered\* by extracting with a dilute solution of HDEHP in an aliphatic hydrocarbon diluent.

Americium and curium may be readily stripped from 0.3 M HDEHP in n-dodecane by 1 N nitric or hydrochloric acid. Stripping with 1 N HNO<sub>3</sub> avoids the use of corrosive chlorides.

This report is an account of progress to date in laboratory studies limited to the two actinides, americium and curium, at tracer levels. Expansion of this study to other actinides and the operation of multi-stage countercurrent systems at higher concentrations will be the subjects of future reports. In this report, the process flowsheet is described as envisaged on the basis of present information. Extraction and stripping data are presented first for the reagents used in the preferred flowsheet, then in later sections for other reagents. Results are included from a multistage test utilizing extraction chromatography, and studies on the behavior of contaminating elements, the effects of irradiation, and corrosion.

## 2. FLOWSHEET

A tentative flowsheet for the separation of americium and curium from the lanthanides and yttrium is shown in Fig. 1. Some modifications would be necessary for processing mixtures containing the transcurium elements. The relative volumes or flow rates (circled numbers) are rough estimates. Preliminary data obtained by Baybarz indicate that californium and einsteinium can be separated from the lanthanides along with americium and curium. The feed to the separation cycle consists of a mixture of the elements in a solution of a carboxylic acid. A suitable solution is about

---

\*It may be possible to recover americium and curium from the raffinate of the lanthanide solvent-extraction cycle by oxalate precipitation. Thus far, sufficient tests have not been made to determine the recoveries and separations from other impurities in the liquor that might be expected from such a process.

1 M in lactic acid, which may contain a considerable concentration of nitrate ion. The scrub is a mixed solution of the same carboxylic acid and diethylenetriaminepentaacetic acid (DTPA), adjusted to about pH 3. Satisfactory conditions can be obtained with a solution 1 M in lactic acid and 0.1 M in pentasodium diethylenetriaminepentaacetate ( $\text{Na}_5\text{DTPA}$ ). The extractant is a dilute solution of di(2-ethylhexyl)phosphoric acid in an aromatic hydrocarbon diluent. A preferred extractant is 0.5 M HDEHP in diisopropylbenzene (DIPB). Fewer than 10 stages in this cycle will give very effective removal of the lanthanides and yttrium without extracting an appreciable amount of americium or curium.

The actinides are recovered from the first-cycle raffinate in a second extraction cycle. (If no impurities other than lanthanides and yttrium are involved, the pure actinide group can be recovered by oxalate precipitation from the first-cycle raffinate. Further, an oxalate precipitation alone might provide adequate decontamination from many impurities, cf. footnote, p. 5.) Extraction of the actinides is accomplished by using a dilute solution of the extractant in a more favorable diluent (0.3 M HDEHP in n-dodecane) and a lower pH, about 1.5. The lower pH also increases the rate of extraction. Still higher extraction power for the actinides could be obtained, if it were needed, by using HEH[ $\phi$ P] instead of HDEHP, but stripping would be more difficult. The second-cycle scrub is similar to the first-cycle scrub, but with lower pH and concentration of complexing agent: 1 M lactic acid, 0.05 M DTPA, pH 1.5. Americium and curium were stripped by 1 N  $\text{HNO}_3$ , with stripping coefficients about 10. Stripping of the heavier actinides would require a more concentrated acid solution. It may be possible to apply this property to a subgroup separation.<sup>3</sup> Another alternative is to use the strip solution containing all the trivalent actinides as feed to the phosphonate process<sup>4</sup> for separating the transcurium elements from americium and curium.

### 3. EXPERIMENTAL

#### 3.1 Materials: Extractants, Diluents, Complexants, and Carboxylic Acid Buffers

The major extractant tested, di(2-ethylhexyl)phosphoric acid, was carefully purified<sup>5</sup> and analyzed. It was free of dibasic organophosphates and was diluted and assayed by titration. Tests with unpurified material showed no effects from impurities on extraction. Supplies of other extractants on hand were too small to justify purification. Diluents were commercial reagents, used as received.

Commercial pentasodium diethylenetriaminepentaacetate (Versenex-80, Na<sub>5</sub>DTPA) was usually used as obtained from Dow Chemical Company. It was a 1.05 M aqueous solution. Material made by crystallizing the acid form and reconverting to the pentasodium salt gave identical results at the same pH values. Sodium salts of hydroxylethylenediaminetriacetic acid (HEDTA), ethylenediaminetetraacetic acid (EDTA) and triethylenetetraminehexaacetic acid (TTHA) were also Dow products. The last of these contained 35% NaCl. Nitrilotriacetic acid (NTA) and 1,2-diaminocyclohexanetetraacetic acid (DCTA) were used as received from Geigy Chemical Corporation. The carboxylic acids used were all standard stockroom chemicals. Where "practical" grades were compared with "pure" grades, there was no difference in results when concentrations of the principal reagent were identical.

#### 3.2 Procedures

Extraction data were obtained by adding tracers in relatively very small volumes to prepared aqueous solutions, contacting the aqueous phases with prepared organic-extractant phases in separatory funnels by hand or mechanical agitation, separating the phases by centrifugation, sampling by pipette into culture tubes and measuring activity by counting in a well-type scintillation gamma counter.

Gamma-emitting tracers used included  $^{241}\text{Am}$ ,  $^{140}\text{La}$ ,  $^{144}\text{Ce}$ ,  $^{142}\text{Pr}$ ,  $^{147}\text{Nd}$ ,  $^{147}\text{Pm}$ ,  $^{153}\text{Sm}$ ,  $^{152}\text{Eu}$ ,  $^{170}\text{Tm}$ , and  $^{91}\text{Y}$ . Curium-242 activities were measured by alpha counting after preparation of plates.

Distribution (extraction) coefficients were the ratios of the activities in corresponding organic and aqueous phases, and separation factors were the ratios of the distribution coefficients of two elements under identical conditions. In some cases pairs of elements were used in the same solutions and measured by standard methods of discrimination.

Many of the data in a series of tests were obtained by first extracting the metal (or metals) into the organic phase and then conducting a series of scrubs by different aqueous solutions. This was possible only when extraction coefficients were high. Data were often checked by making two or more successive scrubs with identical aqueous solutions. Contact times were usually 20 min. This was far more than necessary for reaching equilibrium in most cases. However, in special instances, a slow rate of approach to equilibrium was observed (cf. Sec 4.2.1).

#### 4. RESULTS: EXPERIMENTAL DATA

Most of the experimental work was concerned with extraction by di-(2-ethylhexyl)phosphoric acid, while 2-ethylhexyl phenylphosphonic acid was studied to a lesser extent and other organophosphoric or organophosphonic acids were studied only slightly. After preliminary tests showed that diethylenetriaminepentaacetic acid was the most effective of several aqueous complexing agents studied in causing differences between the two groups of elements, it was given almost exclusive attention. Of several carboxylic acids tested, lactic acid was the one most thoroughly studied after a preliminary survey showed that it had the advantage of better phase separation. Cerium and europium were used as examples of fission-product lanthanides. Subsequent tests showed that some of the intermediate lanthanides are less extractable than europium. Yttrium, an important fission product, and thulium and lutetium, examples of the heavier lanthanides, were tested under only a few conditions.

Data are reported here also from a study of extraction by dialkylphosphoric acids from solutions of various carboxylic acids containing no aminopolyacetic acids.

#### 4.1 First Cycle Extraction: Removal of Lanthanides

##### 4.1.1 Extractions by HDEHP from DTPA in Preferred Aqueous Medium - Lactic Acid

Several lanthanides were compared with americium in extractability by 0.3 M HDEHP in diisopropylbenzene (DIPB) from 1 M lactic acid solutions containing various concentrations of commercial pentasodium diethylenetriaminepentaacetate ( $\text{Na}_5\text{DTPA}$ ). Very small concentrations of  $\text{Na}_5\text{DTPA}$  decreased the extractability of americium very markedly and that of europium somewhat less, but the complexant in small concentrations actually increased the extraction of at least lanthanum and cerium (Fig. 2). Further increases in concentration of  $\text{Na}_5\text{DTPA}$  decreased extractions of all these elements to different extents, so that cerium became slightly more extractable than europium, which became about 100 times more extractable than americium, at a  $\text{Na}_5\text{DTPA}$  concentration of 0.05 M. The intermediate lanthanides were less extractable, neodymium being about half as extractable as europium. Still further increases in  $\text{Na}_5\text{DTPA}$  concentration had little further effect on the relative extractabilities of cerium and europium. Yttrium and thulium were about 4 and 200 times more extractable than cerium when the  $\text{Na}_5\text{DTPA}$  concentration was 0.05 M. These extractions differ slightly from those from solutions containing  $\text{Na}_5\text{DTPA}$  made from recrystallized  $\text{H}_5\text{DTPA}$  (Fig. 3), because of the higher alkalinity of the commercial  $\text{Na}_5\text{DTPA}$  solution.

In extractions by 0.3 M HDEHP in *n*-dodecane from 1 M lactic acid — 0.1 M  $\text{Na}_5\text{DTPA}$  solution, the Eu/Am separation factor was only about 40 (Fig. 4), while the distribution coefficients of cerium and europium were about 5 times as high as in extractions by 0.3 M HDEHP in DIPB. Because of the higher separation factor obtainable, DIPB is preferred to *n*-dodecane as a diluent in the separation cycle.

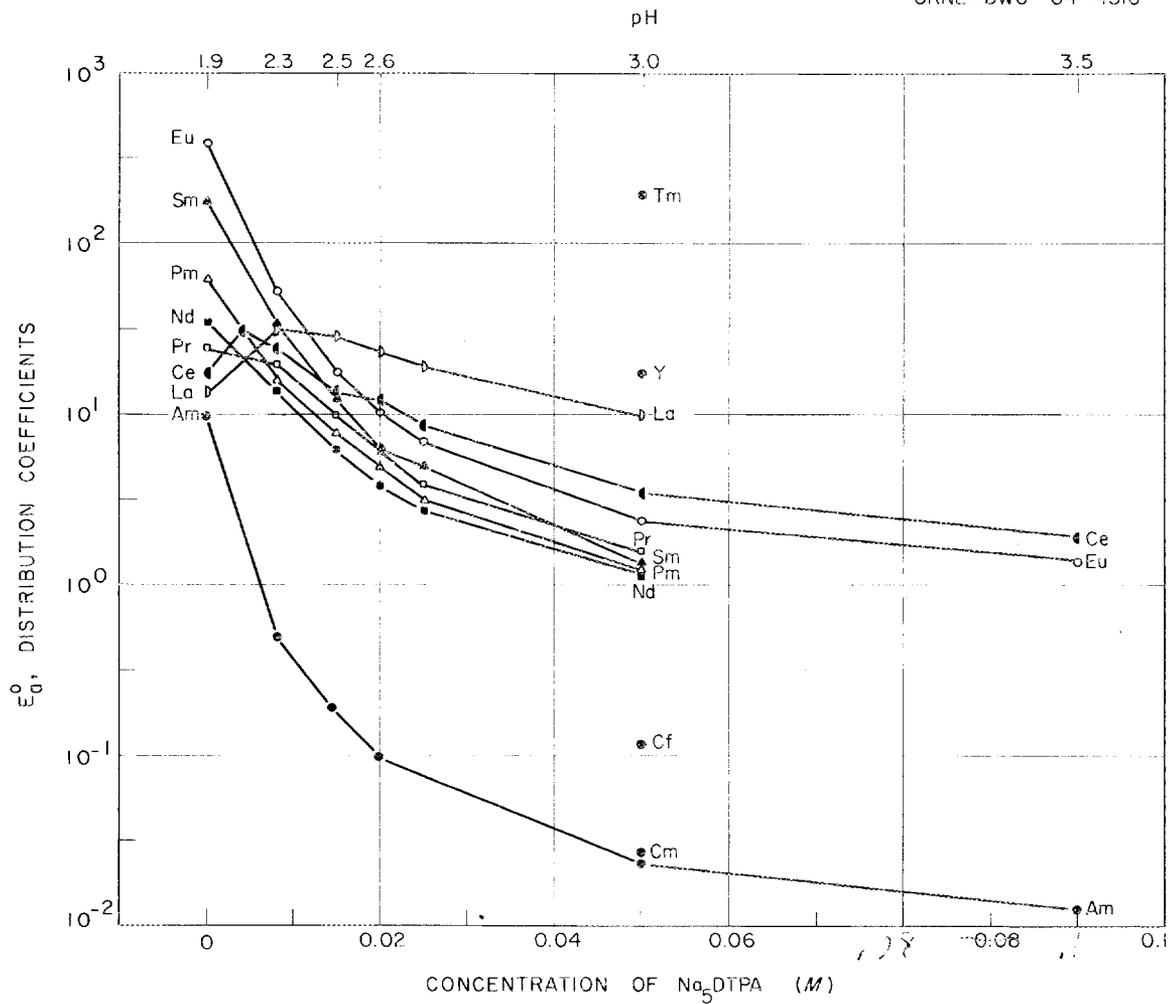
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Fig. 2. DTPA Causes Large Differences in Extraction of Americium and Rare Earths. Extractant: 0.3 M HDEHP in DIBP. Aqueous phase: 1 M lactic acid, variable  $\text{Na}_5\text{DTPA}$  concentration.

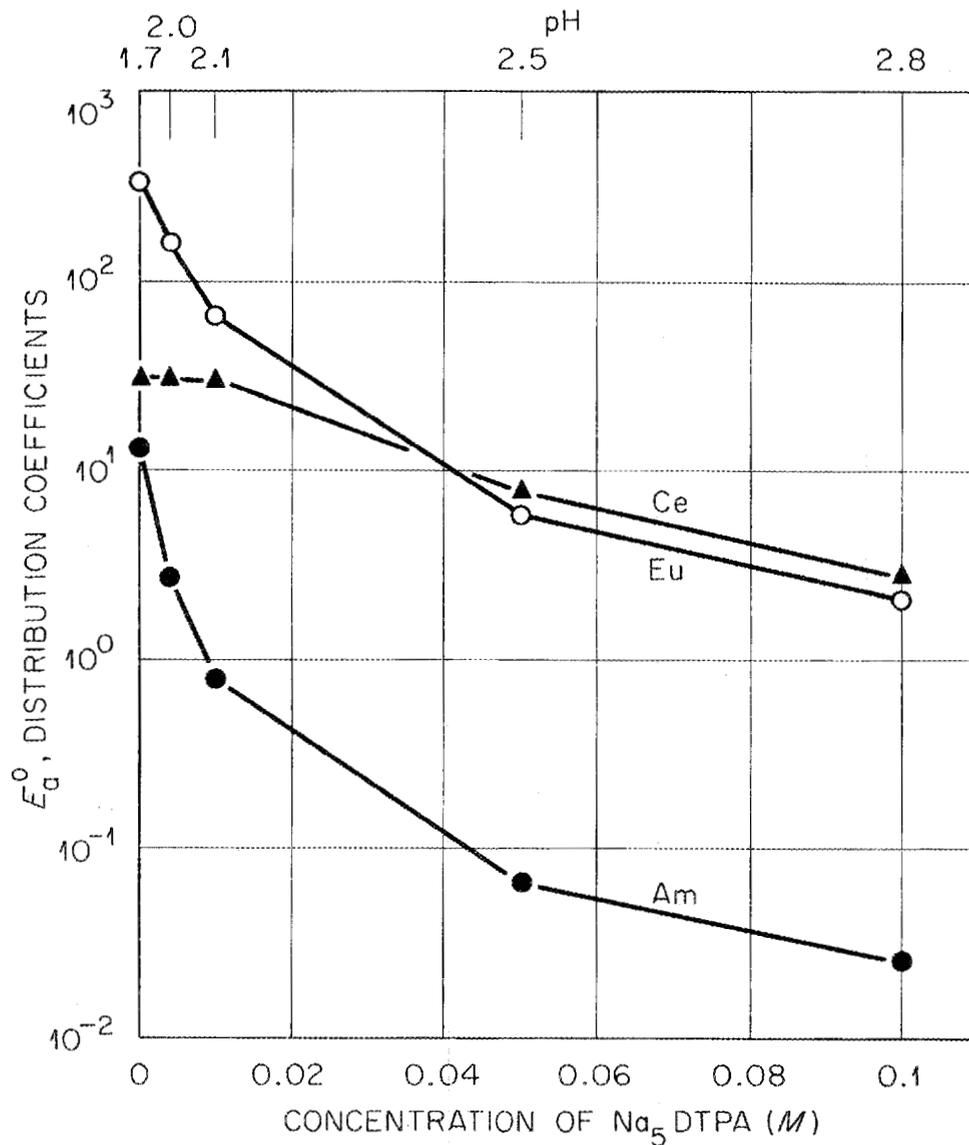
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Fig. 3. Purified DTPA Gives Same Results as Commercial Versenex-80, Except for Shift from pH Difference (*cf.* Fig. 2). Extractant: 0.3  $M$  HDEHP in DIPB. Aqueous phase: 1  $M$  lactic acid, variable  $\text{Na}_5\text{DTPA}$  (purified) concentration.

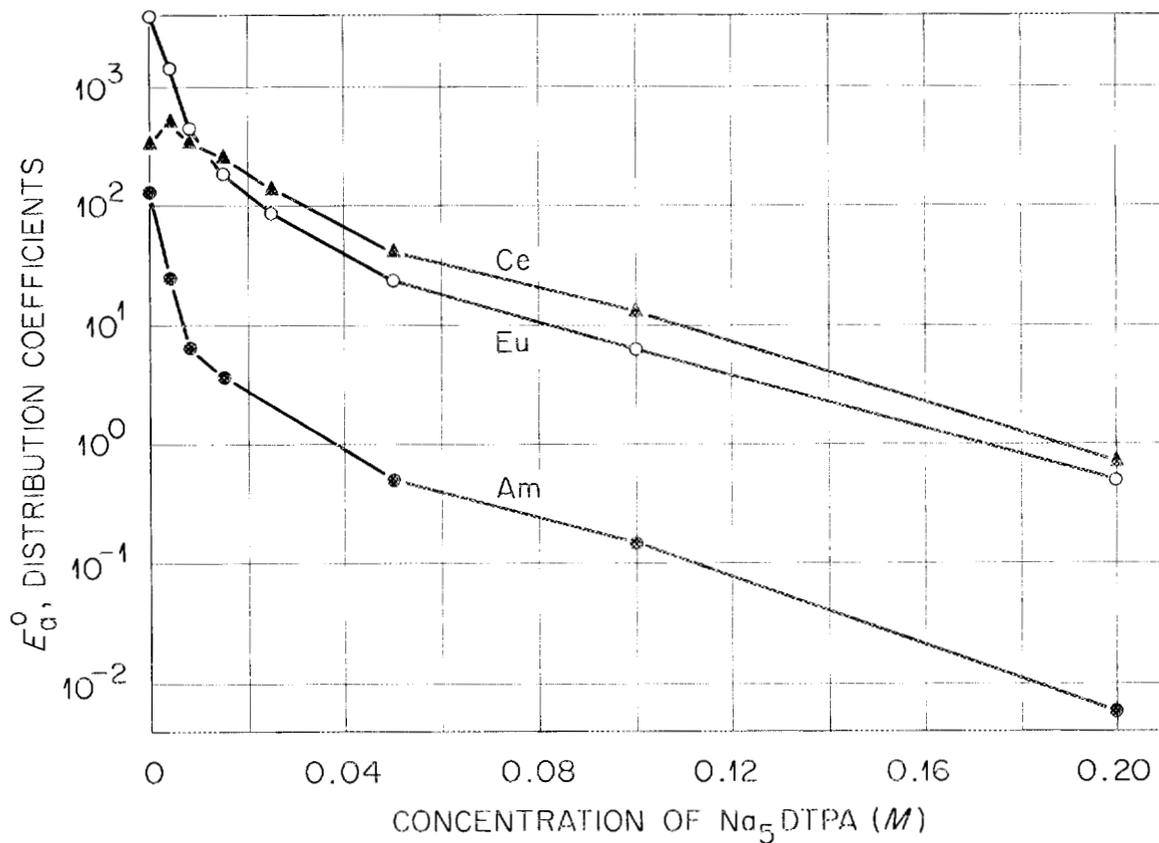
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Fig. 4. Extractions are Much Higher but Separation Lower with  $n$ -Dodecane Diluent than with DIPB (cf. Fig. 2). Extractant: 0.3 M HDEHP in  $n$ -dodecane. Aqueous phase: 1 M lactic acid, variable  $\text{Na}_5\text{DTPA}$  concentration.

#### 4.1.2 Extractions by HDEHP from DTPA in Glycolic Acid

In extractions by 0.3 M HDEHP in DIPB from 1 M glycolic acid containing 1 g of cerium per liter, a Ce/Am separation factor of 100 was obtained when the concentration of Na<sub>5</sub>DTPA was only about 0.05 M (Fig. 5). Cerium and europium were alike at this point. These extractions were somewhat higher than those by 0.3 M HDEHP in diethylbenzene (DEB) from 1 M glycolic acid solutions containing no rare earths beyond the tracer level, especially at low concentrations of Na<sub>5</sub>DTPA (Fig. 6). Part of this difference was a diluent effect, but part was probably caused by decrease of the effective DTPA concentration by the appreciable amount of cerium present. These and other data from extractions from solutions at tracer level (Table 1) or from solutions containing cerium or europium (Table 2) show that the absolute and relative distribution coefficients of the elements are dependent on concentrations of DTPA and glycolic acid and on pH. Increasing the pH increases the complexing power of the DTPA, especially for americium, thus decreasing distribution coefficients and increasing separation factors between the lanthanides and americium. More complexing agent was required to obtain the same separation factors between europium and americium as the concentration of glycolic acid was increased. Americium and curium were very nearly alike wherever they were compared.

#### 4.1.3 Extractions by HDEHP from DTPA in Citric Acid

Extraction by 0.3 M HDEHP in DIPB from citric acid solutions containing Na<sub>5</sub>DTPA also gave large separations between the lanthanides and the americium-curium pair (Table 3). The separation factors at constant concentrations of citric acid and Na<sub>5</sub>DTPA increased as the pH increased. For example, with a concentration of only 0.008 M Na<sub>5</sub>DTPA in 0.5 M citric acid, the Ce/Am separation factor was small at pH 1.8 but increased to nearly 100 when the pH of the aqueous phase was increased to 3.5 (Fig. 7).

#### 4.1.4 Extractions by HDEHP from DTPA in Formic Acid

Tests of extraction by HDEHP solutions from solutions 1 M and 2 M in formic acid gave high but inconsistent coefficients for the elements studied. Consistent results were obtained from solutions 5 M in formic

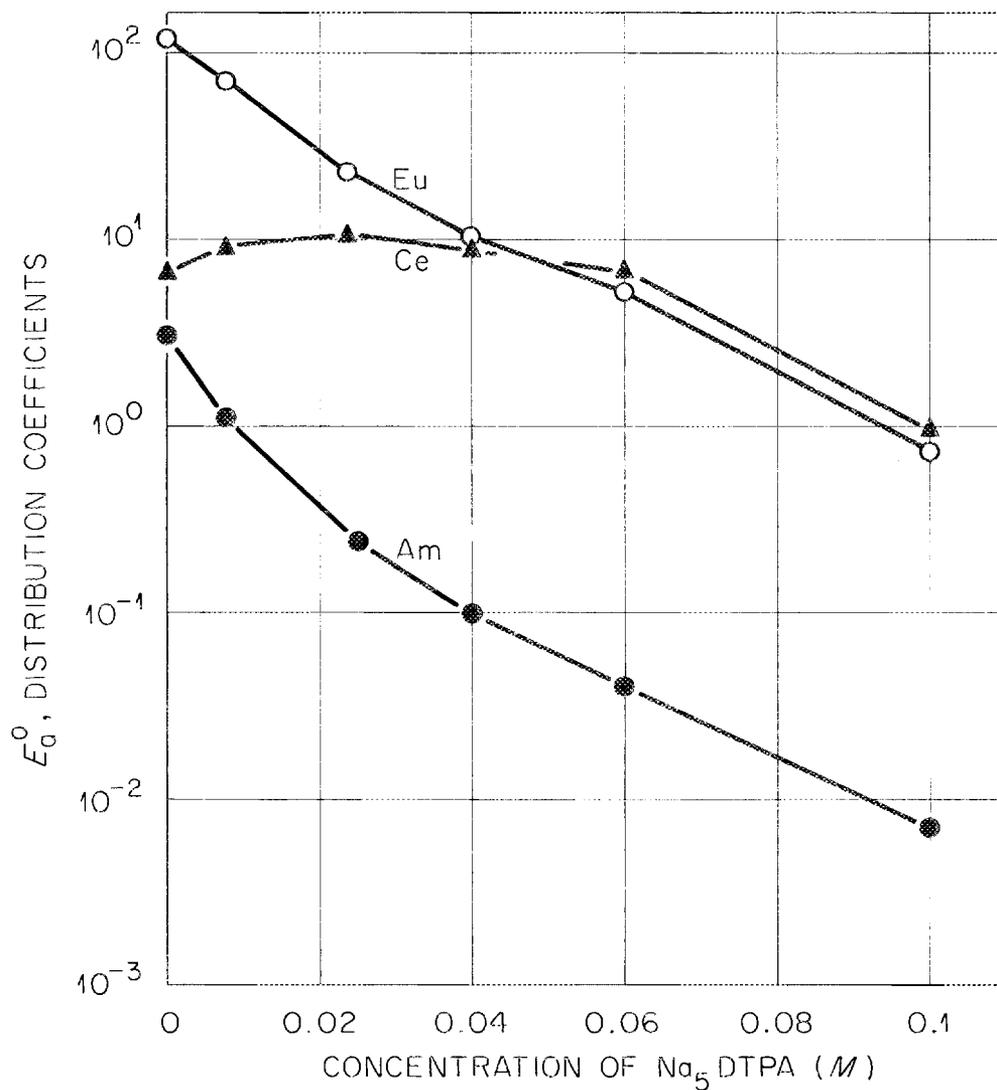
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Fig. 5. Extractions from Glycolic Acid Medium are Similar to those from Lactic Acid (cf. Fig. 2). Extractant: 0.3  $M$  HDEHP in DIPB. Aqueous phase: 1  $M$  glycolic acid, 1 g cerium per liter, variable  $\text{Na}_5\text{DTPA}$  concentration.

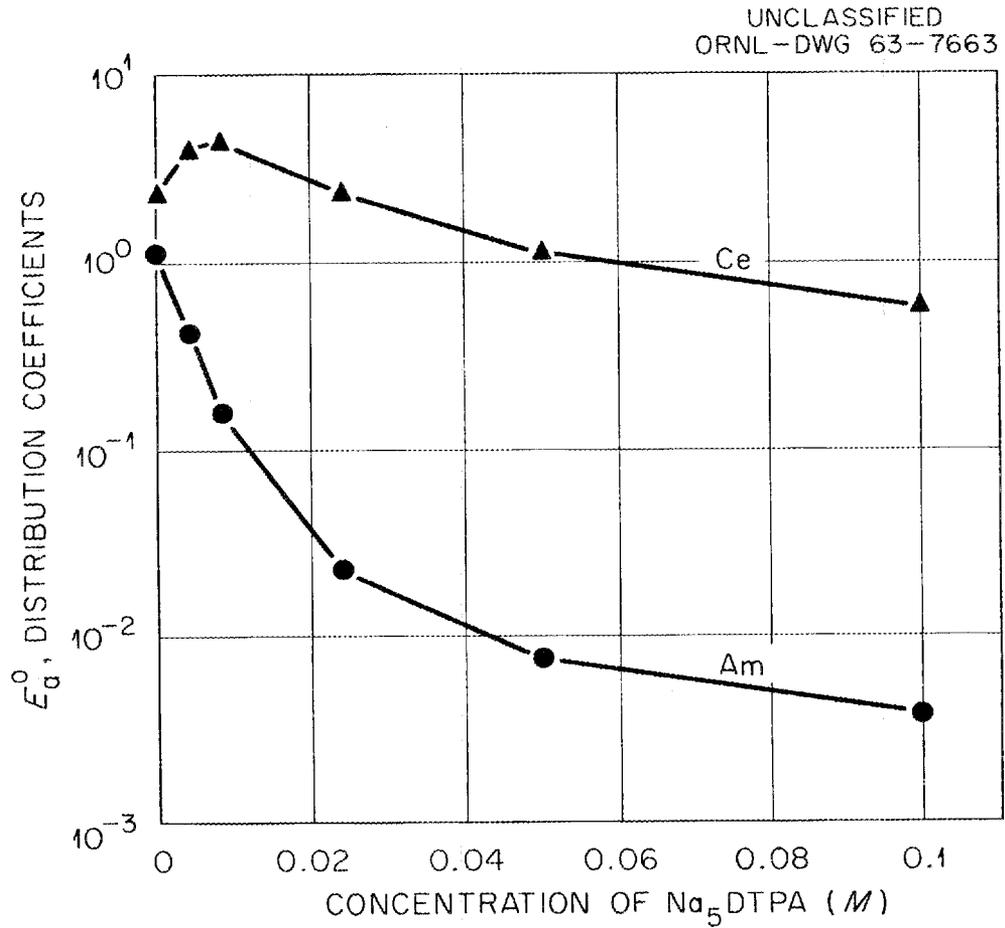


Fig. 6. Extractions are Lower but Separation About Equal with DEB Diluent as with DIPB (cf. Fig. 5). Extractant: 0.3 M HDEHP in DEB. Aqueous phase: 1 M glycolic acid, variable Na<sub>5</sub>DTPA concentration.

Table 1. Extractions by Di(2-ethylhexyl)phosphoric Acid (HDEHP)  
from Glycolic Acid Containing Diethylenetriaminepentaacetic Acid

Organic phase: 0.3 M HDEHP in DIPB

Composition of Aqueous Phase			$E_a^0$				Separation Factors	
Glycolic Acid (M)	Na <sub>5</sub> DTPA (M)	pH	Cm	Am	Ce	Eu	Ce/Am	Eu/Am
0.5	0.008	3.0		0.10	11	11	110	110
0.5	0.008	3.5		0.08	10	8	125	100
0.5	0.025	3.1		0.032	4.3	3.4	130	105
0.5	0.025	3.5		0.028	3.7	2.7	130	95
0.5	0.05	3.5		0.016	2.3	1.6	145	100
1.0	0.004	2.1		2.8	17	150	6	54
1.0	0.008	3.0	0.38	0.27	23	29	85	105
1.0	0.008	2.3	1.2	1.1	17	95	15	85
1.0	0.016	2.5		0.29	17	50	59	170
1.0	0.025	2.8		0.05	4.6	4.7	92	95
1.0	0.025	3.0	0.061	0.071	9.3		130	
1.0	0.025	3.5		0.020	2.4	1.9	120	95
1.0	0.05	3.0		0.020	2.1	1.7	105	85
1.0	0.05	3.5		0.017	1.9	1.5	110	88
1.0	0.10	3.5	0.009	0.008	0.91	0.7	110	85
2.0	0.008	2.0		0.45	4.3	54	10	102

Table 2. Extractions by Di(2-ethylhexyl)phosphoric Acid (HDEHP)  
from Glycolic Acid Containing Cerium or Europium  
and Diethylenetriaminepentaacetic Acid

Organic phase: 0.3 M HDEHP in DIPB

Aqueous phase: 1 M glycolic acid plus Na<sub>5</sub>DTPA

Aqueous-Phase Concentrations		$E_a^0$			Separation Factors	
Ce (g/liter)	Na <sub>5</sub> DTPA (M)	Am	Ce	Eu	Ce/Am	Eu/Am
0.1	0.008	1.3	17	107	13	82
0.1	0.024	0.26	15	24	58	91
0.5	0.008	1.2	13	91	11	76
1.0	0.008	1.1	7.0	79	7	72
1.0	0.024	0.24	11	22	45	90
1.0	0.04	0.098	8.7	10	89	106
1.0	0.06	0.041	6.2	5.5	150	130
$Eu_2O_3$ (g/liter)						
0.05	0.008	1.07	17	103	16	96
0.05	0.024	0.24	14	27	60	112
0.10	0.008	1.3	17	109	13	84
1.0	0.008	1.2	13	77	11	64
1.0	0.024	0.2	9.4	16	47	78
2.0	0.008	0.64	11	48	16	75
2.0	0.024	0.088	8.6	8.4	98	95

Table 3. Extractions by Di(2-ethylhexyl)phosphoric Acid from Citric Acid Containing Diethylenetriaminepentaacetic Acid

Organic phase: 0.3 M in DIBP

Aqueous Phase Concentrations			$E_a^0$				Separation Factors	
Citric Acid (M)	Na <sub>5</sub> DTPA (M)	pH	Cm	Am	Ce	Eu	Ce/Am	Eu/Am
0.5	0.008	1.8	1.8	1.5	6.1	99	4.1	66
0.5	0.008	3.0	0.15	0.15	11	16	73	104
0.5	0.008	3.7	0.14	0.13	12	13	92	98
0.5	0.008	1.8		1.4	7.6	110	5.4	79
0.5	0.10	3.5	0.009	0.010	1.2	1.3	120	130
1.0	0.0076	2.0	0.81	0.77	2.1	35	2.7	45
1.0	0.0076	3.7	0.23	0.17	7.0	15	42	91
1.0	0.008	3.1		0.15	4.3	14	29	90
1.0	0.008	3.5		0.13	5.3	12	42	95
1.0	0.008	1.6	0.72	0.62	1.4	31	2.3	50
1.0	0.025	2.1	0.18	0.19	4.6		24	
1.0	0.025	3.7	0.067	0.074	7.5		100	
2.0	0.008	1.0	0.18	0.10	0.23	5.0	2.3	50
3.0	0.008	1.0	0.043	0.026	0.061	1.3	2.3	50
3.0	0.008	3.0		0.07	0.46	3.0	6.6	43
3.0	0.008	3.5		0.075	0.61	4.8	7.8	56

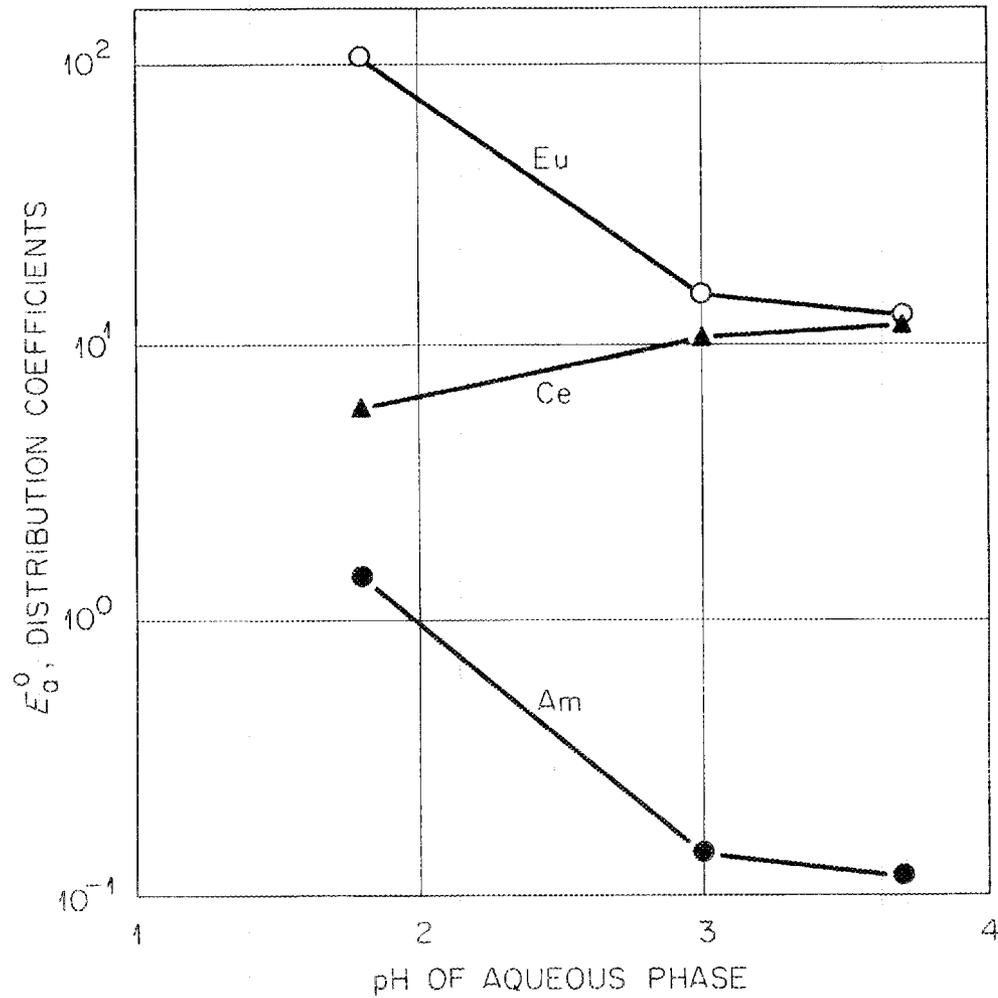
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Fig. 7. Increase of pH Increases Separation by Small Concentration of DTPA. Extractant: 0.3 M HDEHP in DIPB. Aqueous phase: 0.5 M citric acid, 0.008 M  $\text{Na}_5\text{DTPA}$  concentration.

acid, except for a slow approach to equilibrium when no  $\text{Na}_5\text{DTPA}$  was present. With 0.3 M HDEHP in *n*-dodecane, (Ce, Eu)/Am separation factors greater than 100 were reached at a  $\text{Na}_5\text{DTPA}$  concentration of 0.3 M (Fig. 8).

#### 4.1.5 Extractions by HDEHP from DTPA in Glycine Nitrate

A mixed solution of equivalent amounts of glycine (aminoacetic acid) and nitric acid behaves in some ways like a solution of a simple carboxylic acid. Extractions by 0.3 M HDEHP in DIPB from 1 M glycine nitrate containing more than 0.05 M  $\text{Na}_5\text{DTPA}$  gave Ce/Am separation factors of about 100 (Fig. 9). Very small concentrations of  $\text{Na}_5\text{DTPA}$  increased the extractions of both cerium and americium. Further additions of  $\text{Na}_5\text{DTPA}$  caused a much more abrupt decrease of americium extraction than of cerium extraction.

#### 4.1.6 Extractions by HDEHP from DTPA in Miscellaneous Carboxylic Acids

Several other carboxylic acids including acetic, diglycolic, malonic, mandelic, and tartaric acids were tested briefly. Some results of extraction by 0.3 M HDEHP in DIPB are given in Table 4.

#### 4.1.7 Extractions by HDEHP from DTPA in Nitrate Solutions Without a Carboxylic Acid

When 0.3 M HDEHP in DIPB was used to extract americium, cerium, and europium from solutions of  $\text{Na}_5\text{DTPA}$  neutralized with nitric acid to a pH of 2.5, an Eu/Am separation factor of 100 was reached at a  $\text{H}_5\text{DTPA}$  concentration of about 0.05 M (Fig. 10). Cerium was slightly more extractable than europium. However, these data were obtained from experiments utilizing 45-min contacts. Several tests with shorter contact periods indicated that equilibrium in the extraction of europium was ordinarily not attained within 30 min, while 5-min contacts were sufficient and probably unnecessarily long for equilibration in the extraction of cerium. There may have been a small time effect in the extraction of americium, but its low extractability made this difficult to observe.

The slowness of extraction of at least some of the rare earths proves a serious handicap to the use of systems which contain no carboxylic acids. Furthermore, the presence of carboxylic acids has other advantages, such

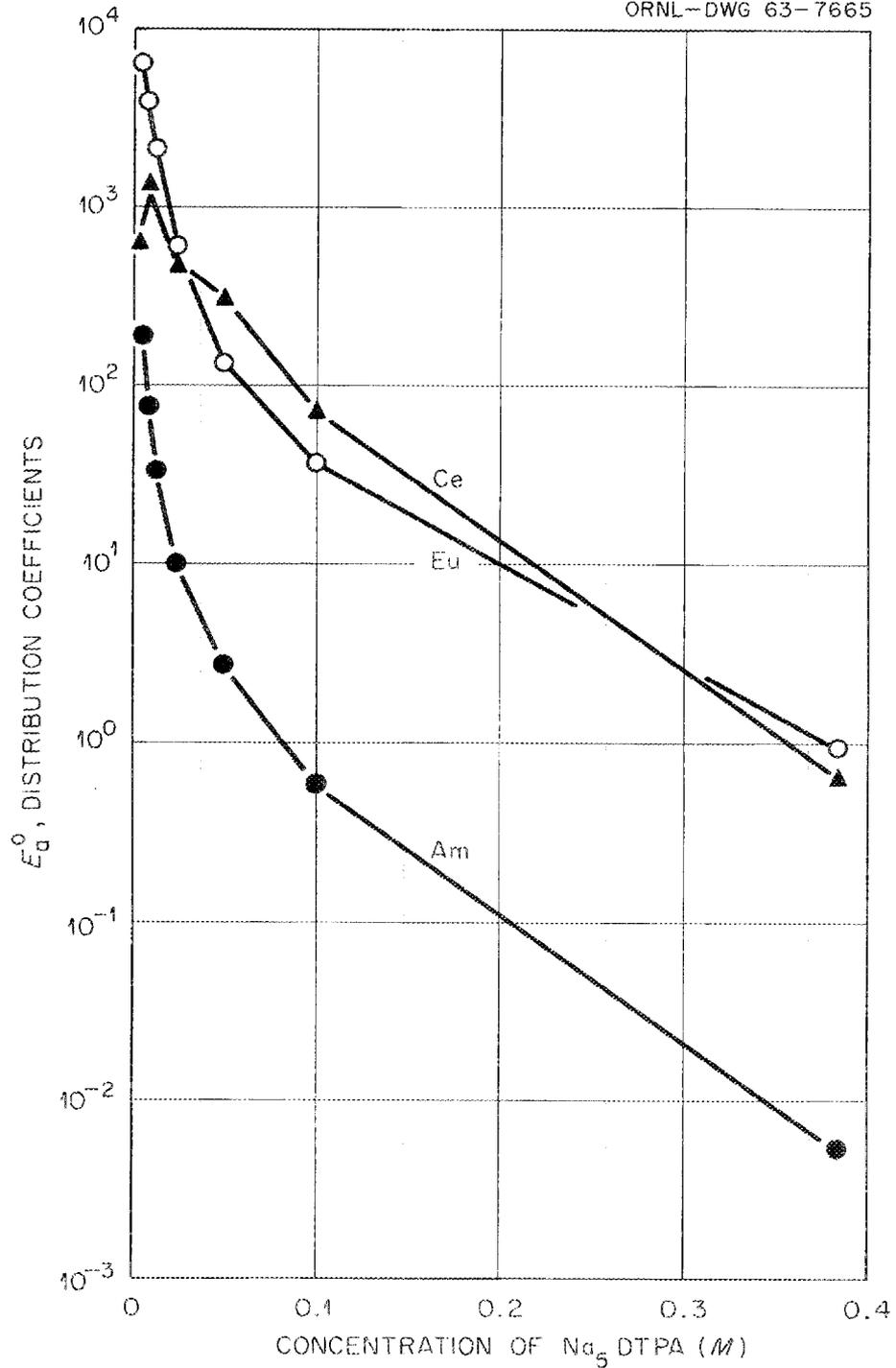
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Fig. 8. DTPA Gives Good Separations in Concentrated Formic Acid Medium. Extractant: 0.3 M HDEHP in *n*-dodecane. Aqueous phase: 5 M formic acid, variable  $\text{Na}_5\text{DTPA}$  concentration.

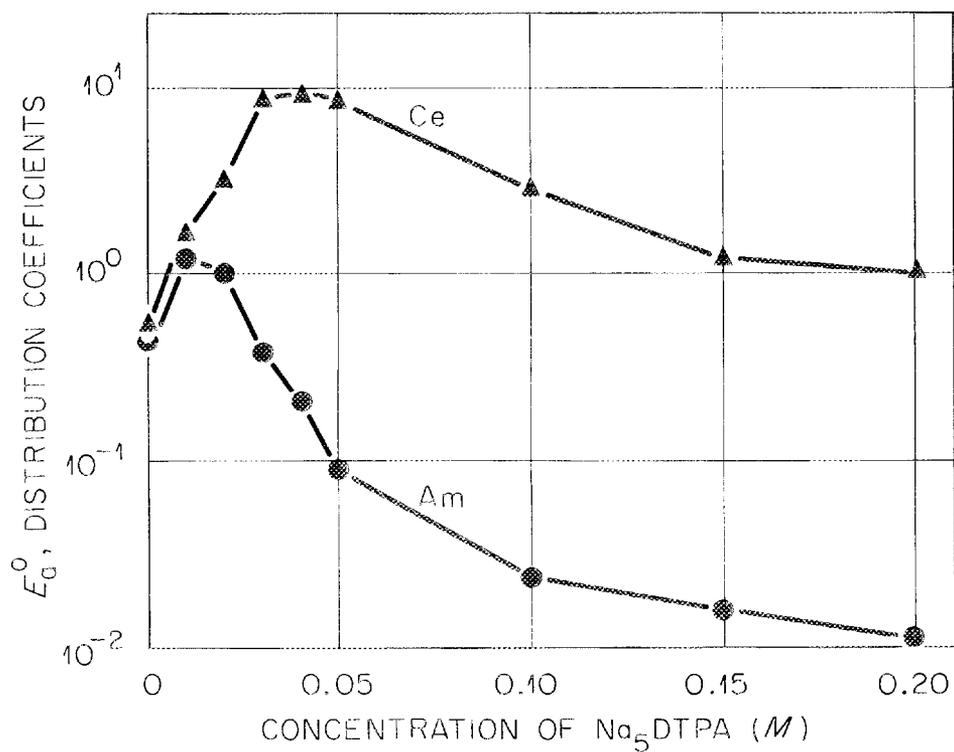
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Fig. 9. DTPA Gives Good Separation in Glycine Nitrate Medium.  
Extractant: 0.3  $M$  HDEHP in DIPB. Aqueous phase: 1  $M$  glycine nitrate,  
variable  $\text{Na}_5\text{DTPA}$  concentration.

Table 4. Extractions by Di(2-ethylhexyl)phosphoric Acid from Solutions of Various Carboxylic Acids Containing Diethylenetriaminepentaacetic Acid

Extractant: 0.3 M HDEHP in DIPB

Aqueous Phase	Na <sub>5</sub> DTPA (M)	pH	E <sub>a</sub> <sup>o</sup>			Separation Factors	
			Am	Ce	Eu	Ce/Am	Eu/Am
0.5 M Tartaric acid	0.008	3.0	0.20	20	20	100	100
0.5 M Tartaric acid	0.008	2.1	1.1	3.9	69	3.5	63
0.5 M Tartaric acid	0.016	3.0	0.11	11	11	100	100
1 M Diglycolic acid	0.0	1.5	0.016	0.071	0.48	4.4	30
1 M Diglycolic acid	0.008	1.7	0.0035	0.075	0.39	21	111
2 M Acetic acid	0.0025		1.0	20	9.1	20	8.8
2 M Acetic acid	0.125		0.17	12	0.96	72	5.7
4 M Acetic acid	0.0076		0.45	17	2.0	37	4.3
4 M Acetic acid	0.0076		0.13	13	2.9	103	23
6 M Acetic acid	0.0076		0.52	67	10	128	38
0.5 M Mandelic acid	0.05	3.3	0.047	5.6	1.4	120	30
0.5 M Mandelic acid	0.10	3.8	0.0051	0.53	0.19	103	37
1 M Malonic acid	0.10	2.7	0.029	2.86	2.52	98	87

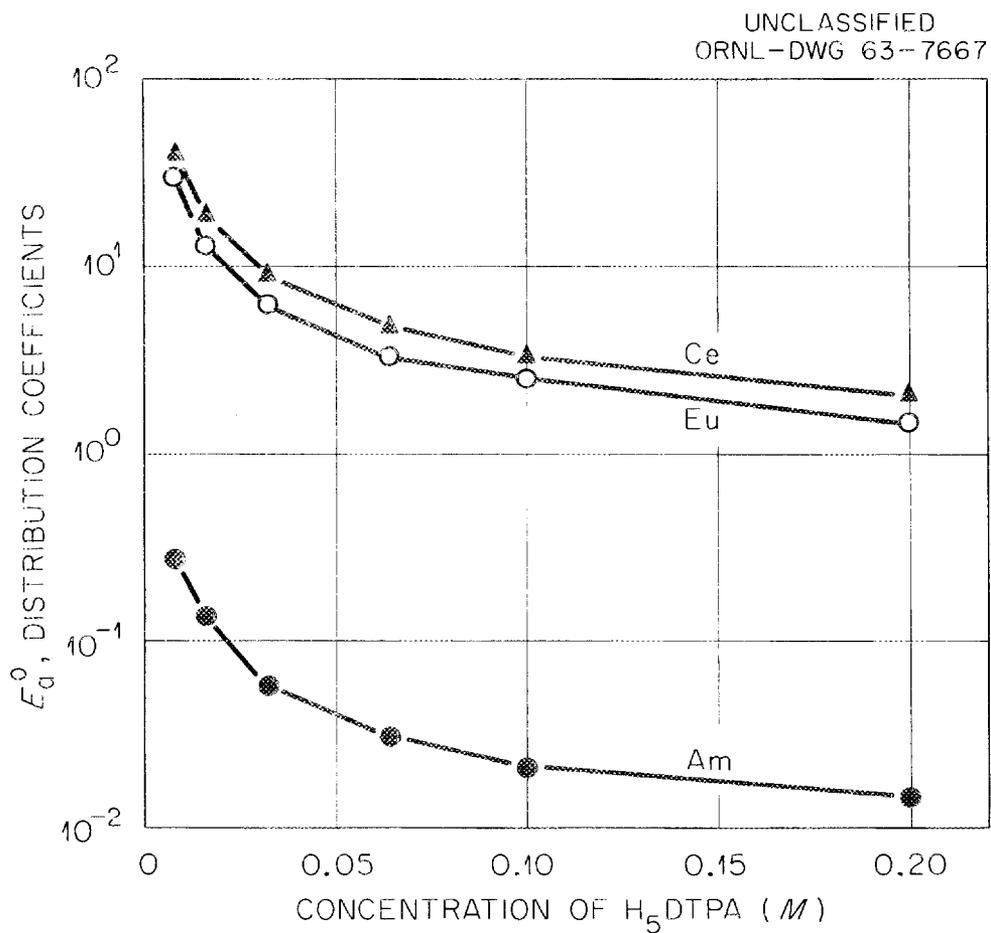


Fig. 10. DTPA Gives High Separations Without a Carboxylic Acid.  
Extractant: 0.3 M HDEHP in DIPB. Aqueous phase: variable  $H_5DTPA$  concentration plus equivalent  $NaNO_3$ , pH 2.5.

as providing a highly buffered aqueous phase and increasing the solubility of  $H_5DTPA$ . Crystals of  $H_5DTPA$  have been observed to form in aged solutions containing originally 0.1  $M$   $H_5DTPA$  and 0.5  $M$   $NaNO_3$ .

#### 4.1.8 Extractions by HDEHP from DTPA in Carboxylic-Aminopolycarboxylic Acid Solutions Containing Nitrate

The preparation of feed for the separation process may be much simpler if nitrates present from previous processing may be left in the solution. In comparative tests of extraction from solutions 1  $M$  in lactic acid and 0.05  $M$  in  $Na_5DTPA$  with similar solutions also 1  $M$  in sodium nitrate, the sodium nitrate decreased coefficients by not more than 20% and gave identical Eu/Am separation factors and slightly higher Ce/Am separation factors. It is evident that the presence of a neutral nitrate up to a concentration of 1  $M$  would not interfere with the separation.

### 4.2 Second-Cycle Extraction and Stripping: Recovery of Actinides

There should be several combinations of extractants and diluents suitable for extracting americium and curium from the aqueous solutions left after removal of the lanthanides, since (1) extractions of trivalent lanthanides and actinides by monoacidic organophosphorus reagents from mineral acids are usually proportional to about the third power of the free reagent concentration, (2) different reagents differ in relative extraction power (for example, 2-ethylhexyl phenylphosphonic acid (HEH[ $\phi$ P]) is a stronger extractant than di(2-ethylhexyl)phosphoric acid (HDEHP), and (3) extractants give higher extractions when dissolved in aliphatic diluents than when dissolved in aromatic diluents. A study of the behavior of several possible systems showed that the actual situation is somewhat more complex than expected. However, satisfactory extraction methods have been developed.

#### 4.2.1 Slowness of Extraction: Solution of Problem

One notable feature of this extraction method as applied to trivalent actinide extraction is the fact that extraction is sometimes slow, regardless of the degree of agitation in the mixing of phases.

In the study of extraction of lanthanides (under conditions suitable for their removal) slow extraction was observed in only a few instances and affected only the heavier lanthanides. It did not interfere with the group separation. As conditions were altered to provide for high extraction of americium, this element was found to extract only slowly under the organic-phase conditions that gave its maximum equilibrium extraction. Over several sets of extraction conditions, extraction was slower by HEH[ $\phi$ P] than by HDEHP, was slower with more concentrated solutions of either extractant, and was slower when the diluent was dodecane than when it was DIPB.

Under the desired organic-phase conditions, americium extraction was too slow for the efficient operation of a multistage system using either HDEHP or HEH[ $\phi$ P]. Extraction of americium by 0.3 M HDEHP in DIPB from a 1 M lactic acid, 0.05 M or 0.10 M Na<sub>5</sub>DTPA solution reached equilibrium in less than 1 min, but the distribution coefficient was too low for use in recovery (Fig. 11). Increasing the concentration of HDEHP to 1 M gave a somewhat higher distribution coefficient (still less than 1), but increased the equilibration time to more than 10 min. Replacement of DIPB with n-dodecane gave a usefully high distribution coefficient (about 3) but did not speed up the extraction. Increasing the Na<sub>5</sub>DTPA concentration to 0.1 M simply decreased the distribution coefficients with both diluents.

Extraction by 1 M HEH[ $\phi$ P] in DIPB from 1 M lactic acid—0.05 M Na<sub>5</sub>DTPA was slower than that by 0.3 M HEH[ $\phi$ P] (Fig. 12). Increasing the Na<sub>5</sub>DTPA concentration to 0.1 M retarded extraction still further, while decreasing the equilibrium distribution coefficient by a factor of 2.5. With n-dodecane instead of DIPB as diluent, distribution coefficients were somewhat higher and the rates were slightly lower (Fig. 13).

Increasing the aqueous acidity accelerated the extraction, presumably because the effectiveness of the aqueous complexing agent is decreased at lower pH. The acidity was increased in two ways, with lactic acid and (preferred) with nitric acid. With lactic acid, equilibrium in extraction by 0.3 M HEH[ $\phi$ P] in n-dodecane from 4 M lactic acid—0.05 M Na<sub>5</sub>DTPA was reached in less than 5 min, and extraction by 1 M HEH[ $\phi$ P]

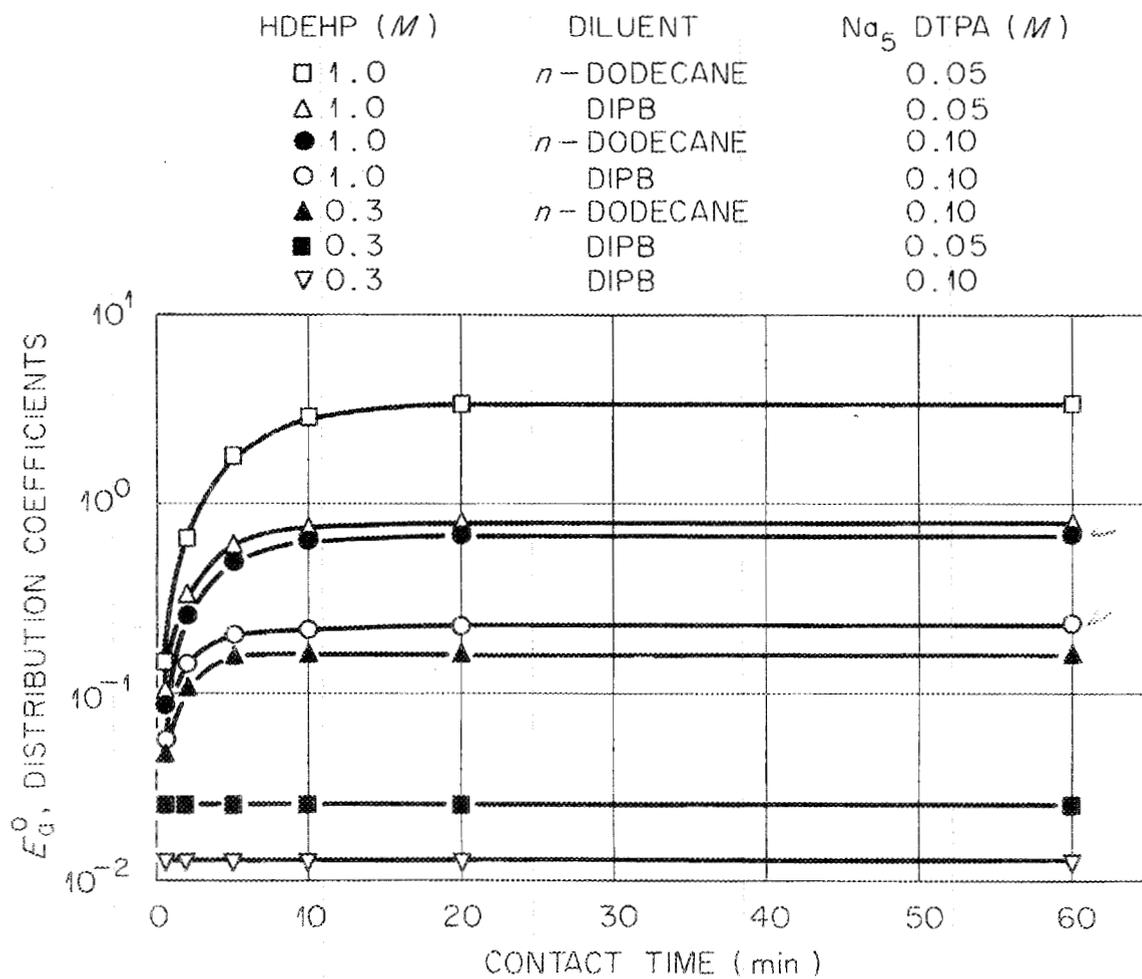
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Fig. 11. Increasing Extractability of Americium with HDEHP Decreases Rate of Extraction. Aqueous phase: 1 M lactic acid plus Na<sub>5</sub>DTPA.

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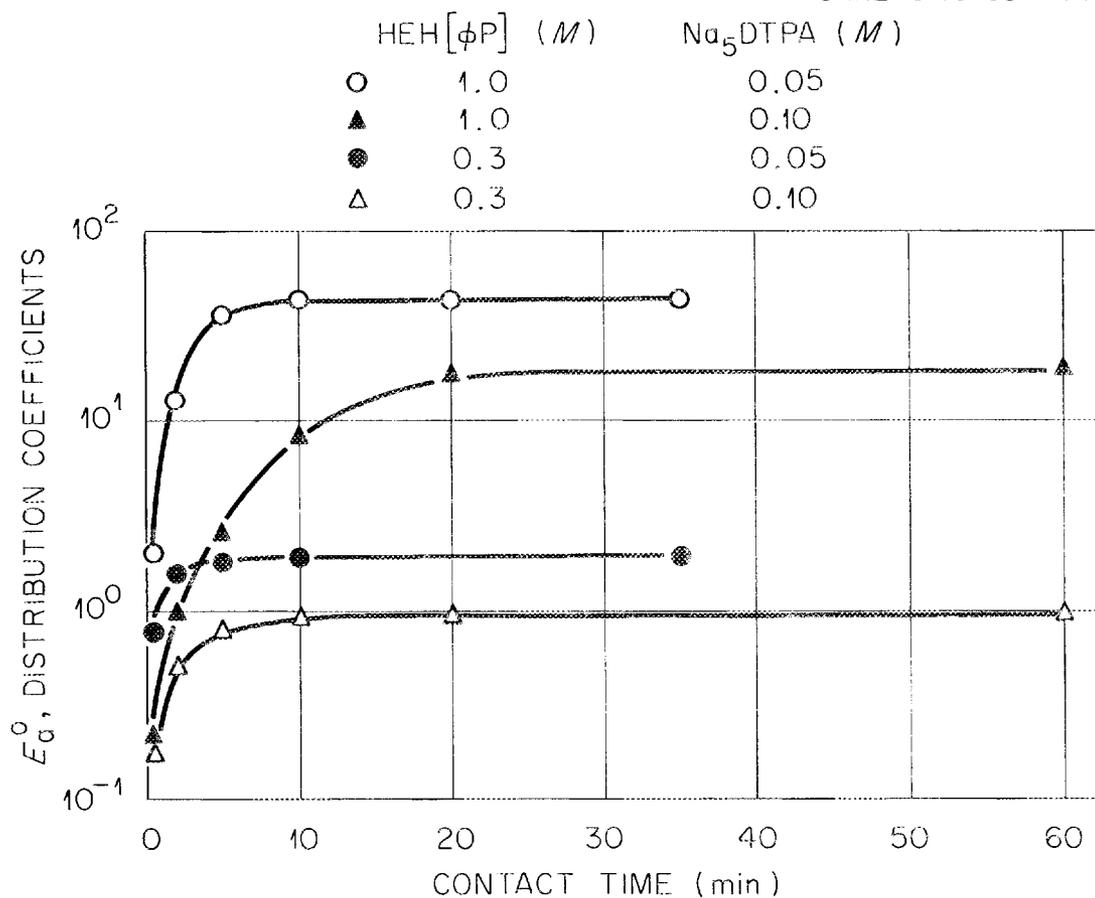


Fig. 12. Increasing Extraction of Americium by HEH[ $\phi$ P] in DIPB Decreases Rate of Extraction. Aqueous phase: 1 M lactic acid plus Na<sub>5</sub>DTPA.

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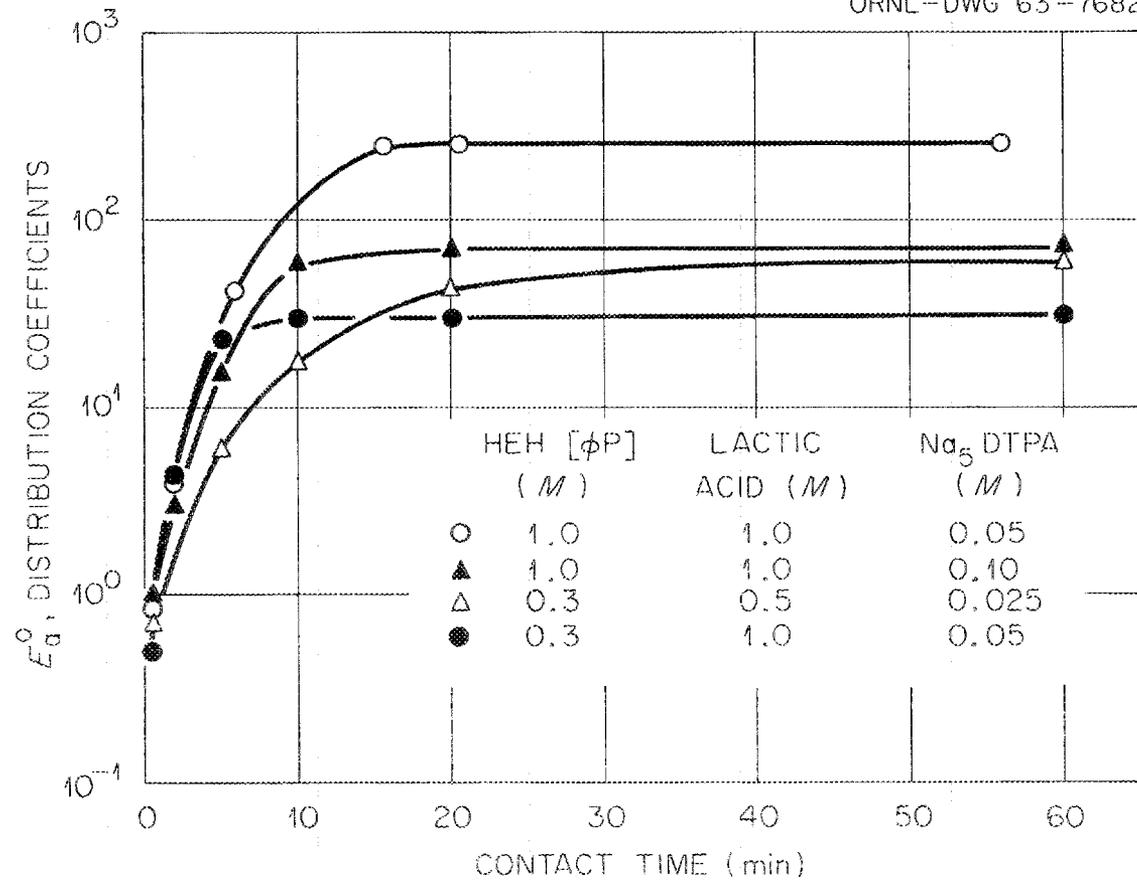


Fig. 13. Increasing Extraction of Americium by HEH[ $\phi$ P] in n-Dodecane Decreases Rate of Extraction.

in n-dodecane from the same aqueous solution reached equilibrium within the shortest measured time (Fig. 14). Distribution coefficients were high enough with only 0.3 M HEH[ $\phi$ P] that a slight deficiency from equilibrium would be of no significance. However, the suitability of this method is in question because it increases the solubility of the extractant in the aqueous phase. When the aqueous phase was 6 M in lactic acid at a pH of 2.5, the solubility of HEH[ $\phi$ P] was sufficient to cause a 20% reduction in the volume of the organic phase. The solubility decreased as pH and concentration of lactic acid were decreased, but it has not yet been determined whether there can be a concentration of lactic acid sufficient to prevent slow extraction without causing excessive solubility of the extractant in the aqueous phase. This solubility was observed only in the case of HEH[ $\phi$ P].

When the aqueous acidity was increased by means of nitric acid, adjustment to pH 0.8 gave equilibration within the shortest measured time in the extraction of americium by 1 M HDEHP in dodecane from a solution initially 0.5 M in lactic acid, 0.025 M in  $\text{Na}_5\text{DTPA}$ , 3 M in sodium nitrate, and 0.09 M in citric acid. The distribution coefficient was 23. A pH of 0.8 was not optimum for high extraction: Increasing the pH changed the coefficient to 100 at pH 1.2, 120 at pH 1.6, and 42 at pH 1.95. In this pH range, equilibrium was always reached within 30 sec. In other tests with various concentrations of nitrate and acids, there was a similar pattern of results, indicating maximum extraction at about pH 1.5 (Figs. 15 and 16). Nitrate ion in excess of the nitric acid used in adjusting the pH had no noticeable effect on distribution coefficients or rates of extraction. Distribution coefficients were higher with 0.01 M  $\text{Na}_5\text{DTPA}$  than with 0.05 M  $\text{Na}_5\text{DTPA}$  only in the middle pH range. (Citric acid was included to increase the solubility of the DTPA; cf. Sec 4.1.3.) Distribution coefficients at pH 1.5 are so high that a dilute solution of HDEHP gives adequate extraction; for example, 0.3 M HDEHP in n-dodecane extracted Am from 1 M lactic acid—0.05 M  $\text{Na}_5\text{DTPA}$  at pH 1.5 with a coefficient of about 10.

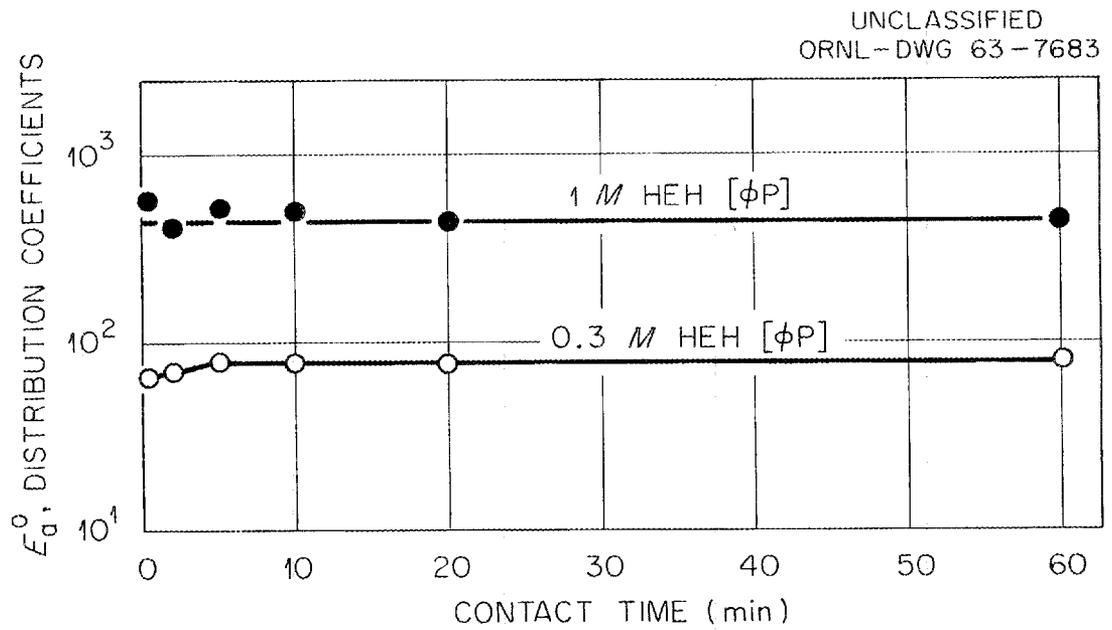


Fig. 14. Increasing Concentration of Lactic Acid Increases Rate of Extraction of Americium by HEH[ $\phi P$ ]. Aqueous phase: 4 M lactic acid, 0.05 M Na<sub>5</sub>DTPA.

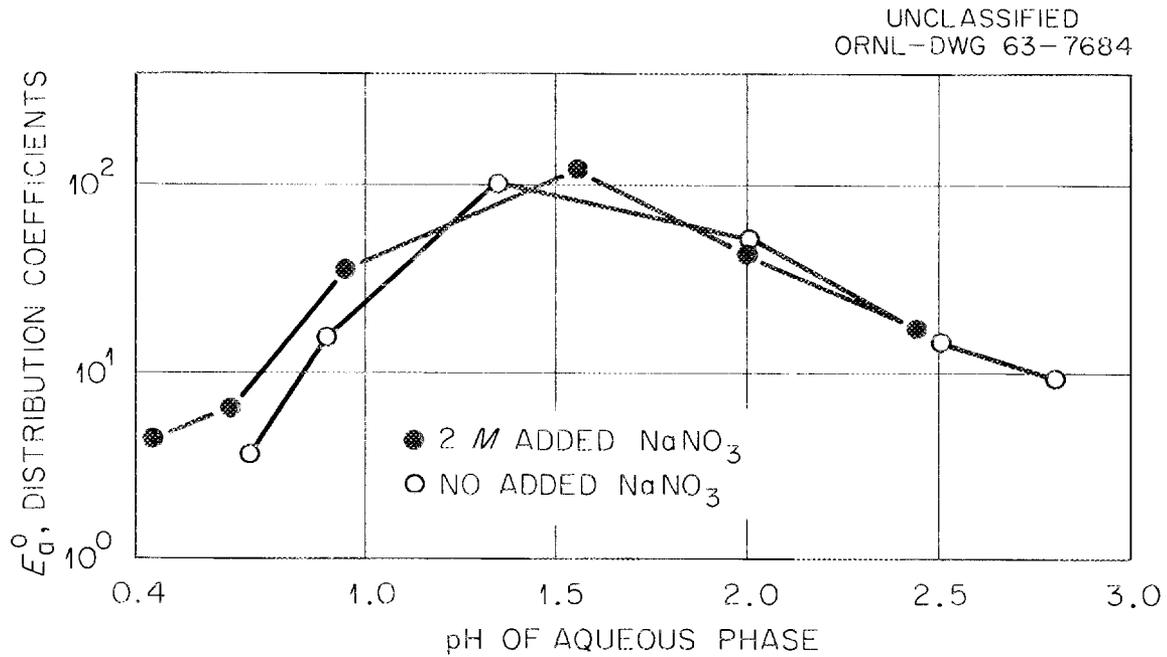


Fig. 15. Extraction of Americium with HDEHP is Maximum at pH about 1.5 and Nearly Independent of  $\text{NaNO}_3$  Concentration. Extractant: 1 M HDEHP in n-dodecane. Aqueous phase: 1 M lactic acid, 0.09 M citric acid, 0.05 M  $\text{Na}_5\text{DTPA}$ , adjusted with  $\text{HNO}_3$ .

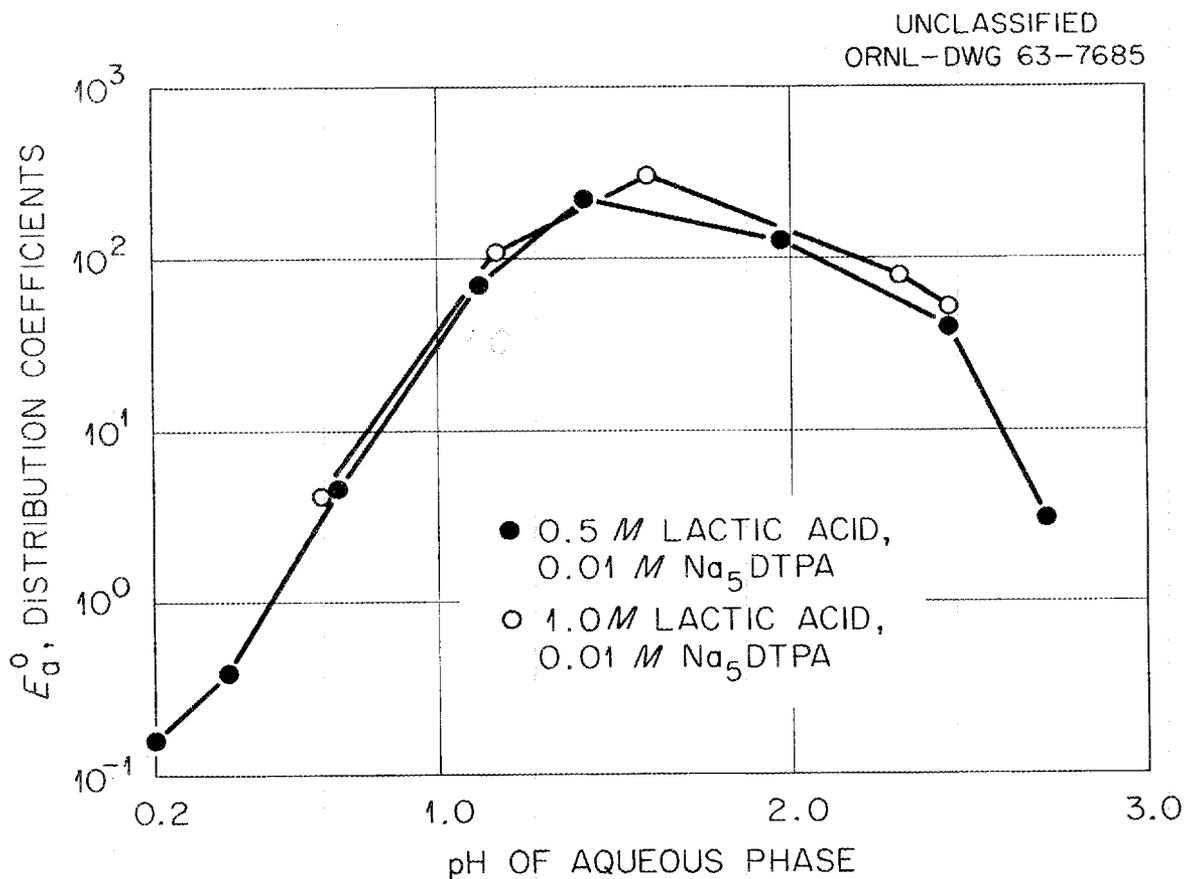


Fig. 16. Extraction of Americium with HDEHP in n-Dodecane is Maximum at pH about 1.5 and Nearly Independent of Lactic Acid Concentration. Extractant: 1 M HDEHP in n-dodecane. Aqueous phase: lactic acid, 0.01 M  $\text{Na}_5\text{DTPA}$ , adjusted with  $\text{HNO}_3$ .

#### 4.2.2 Dependence of Extractions on Extractant Concentration

If distribution coefficients of the trivalent actinides and lanthanides were proportional to a constant power of the free extractant concentration, as is true in extraction by HDEHP from mineral acids (third power), it should be possible to calculate all the extraction coefficients obtainable in each specific system as soon as the coefficient for one extractant concentration is known. However, the power dependence is not constant in these systems. In extractions of americium, cerium, and europium by solutions of HDEHP in DIPB, the extractant concentration power dependence varied between about 2.6 and 2.9 (Fig. 17). Data from the extraction rate study reported above (Sec 4.2.1) indicate a slightly lower power dependence for extraction by HEH[ $\phi$ P] in DIPB, a decrease to 1.8 on substitution of *n*-dodecane for DIPB, and a further decrease to 1.4 when the lactic acid concentration was increased from 1 M to 4 M (Fig. 18). Thus, distribution coefficients cannot be predicted without detailed information on the compositions of both phases and the effects of composition variables on extractant concentration dependence.

#### 4.3 Multistage Test by Extraction Chromatography

A multistage test of the 1 M glycine nitrate—DTPA system was performed by utilizing extraction chromatography. A 5-ml volume of 0.3 M HDEHP in DIPB was absorbed in 5 g of microporous polyethylene granules (30 to 40 mesh), supplied by Winsten Laboratories. The apparently dry granules were then immersed in water and packed into a tube of about 1-cm<sup>2</sup> cross section, with a Pyrex-wool plug and cover and a stopcock at the bottom. The height of the packed column was about 20 cm. A 10-ml volume of solution containing a mixture of <sup>144</sup>Ce and <sup>241</sup>Am tracers and 1 M in glycine nitrate and 0.05 M in Na<sub>5</sub>DTPA was poured into the tube and allowed to drain through the column at a rate of about 1 ml/min. Residual solution was washed down the column by small volumes of a similar aqueous solution without tracers, followed by a further flow of the same until <sup>241</sup>Am was absent from the effluent. The effluent was collected in successive 5-ml volumes, which were then analyzed. The first 75 ml contained no <sup>144</sup>Ce, while the <sup>241</sup>Am was eluted sharply and

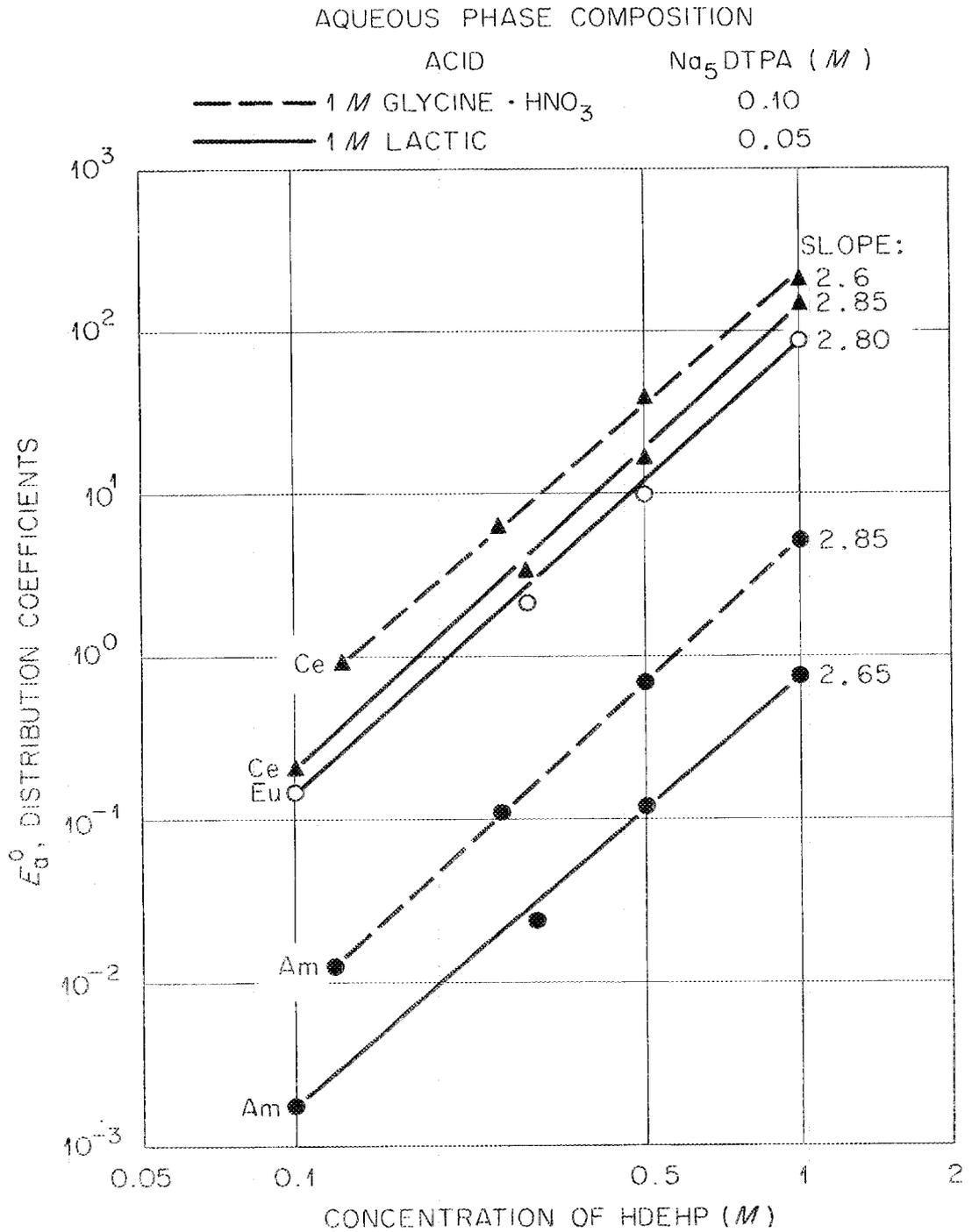
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Fig. 17. Extractions by HDEHP in DIPB Are Proportional to Nearly the Third Power of the Extractant Concentration.

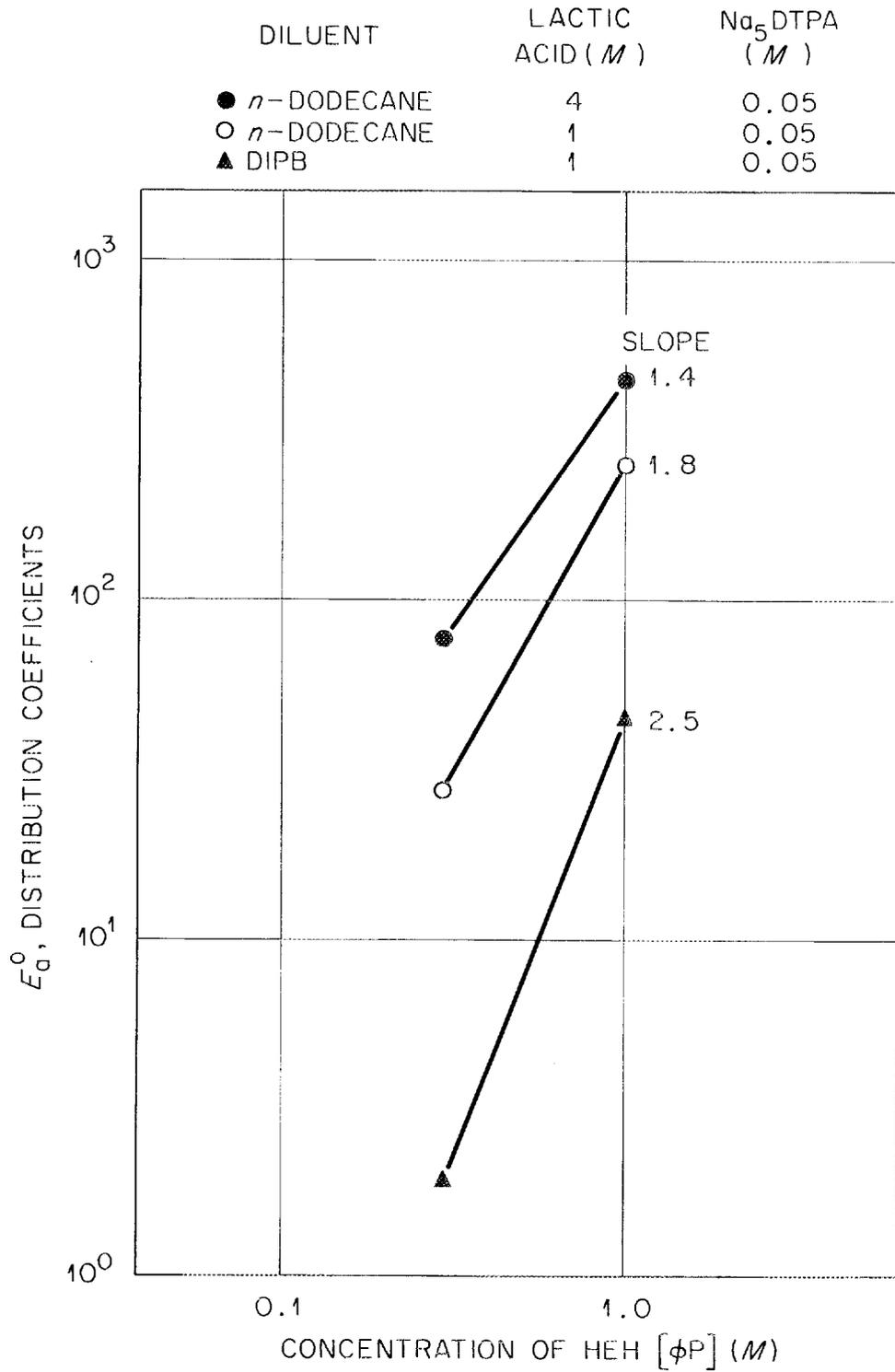


Fig. 18. Reagent Concentration Dependence of Extraction can Vary with Extraction Conditions.

cleanly (Fig. 19). Washing with 1 N HNO<sub>3</sub> removed the <sup>144</sup>Ce in an additional 50-ml volume. Before removal of the <sup>144</sup>Ce, monitoring of the tube showed that the point of maximum <sup>144</sup>Ce activity had moved down about one-third the height of the column.

#### 4.4 Extraction of Other Contaminating Elements

A study was made of the extraction of several elements which might be expected to occur with americium and curium as impurities derived from irradiated target materials, fission, or corrosion of process equipment. Thus far, the study has extended only to extractions by solutions of HDEHP in DIPB from aqueous solutions of glycolic acid and glycine nitrate with and without DTPA. Results are not to be interpreted as applicable to other chemical systems such as extraction by phosphonic acids or from aqueous solutions containing other carboxylic acids.

Data on extraction by 0.3 M HDEHP in DIPB from solutions 1 M in glycolic acid and in glycine nitrate are compiled in Table 5. Extractions of several elements were so small under all conditions tested that they would certainly be left in the aqueous phase through both the lanthanide-removal and the actinide-extraction cycles. These include nickel, cobalt, aluminum, copper, cadmium, lead, tin(II) and iron(III). Though DTPA increased extraction of silver, strontium, chromium(III), and manganese(II) from glycolic acid, they also would probably be left in the first-cycle aqueous solution. Their fate in the second cycle is unpredictable. The extraction of zinc would be very low in the first cycle, but might be appreciable in the second, where the concentration of DTPA is lower.

A distribution coefficient of 65 for zirconium-niobium from 1 M glycolic acid was reduced to about 0.01 when the DTPA concentration was 0.025 M. In the presence of even a very small concentration of natural zirconium, there was almost complete precipitation of the activity. Extraction of ruthenium was very slow, with equilibrium times greater than 1 hr. Distribution coefficients with 30-min contacts did not exceed 0.01. Barium was completely precipitated in attempts to extract it from glycolic acid, and it was partially precipitated when the aqueous phase contained DTPA.

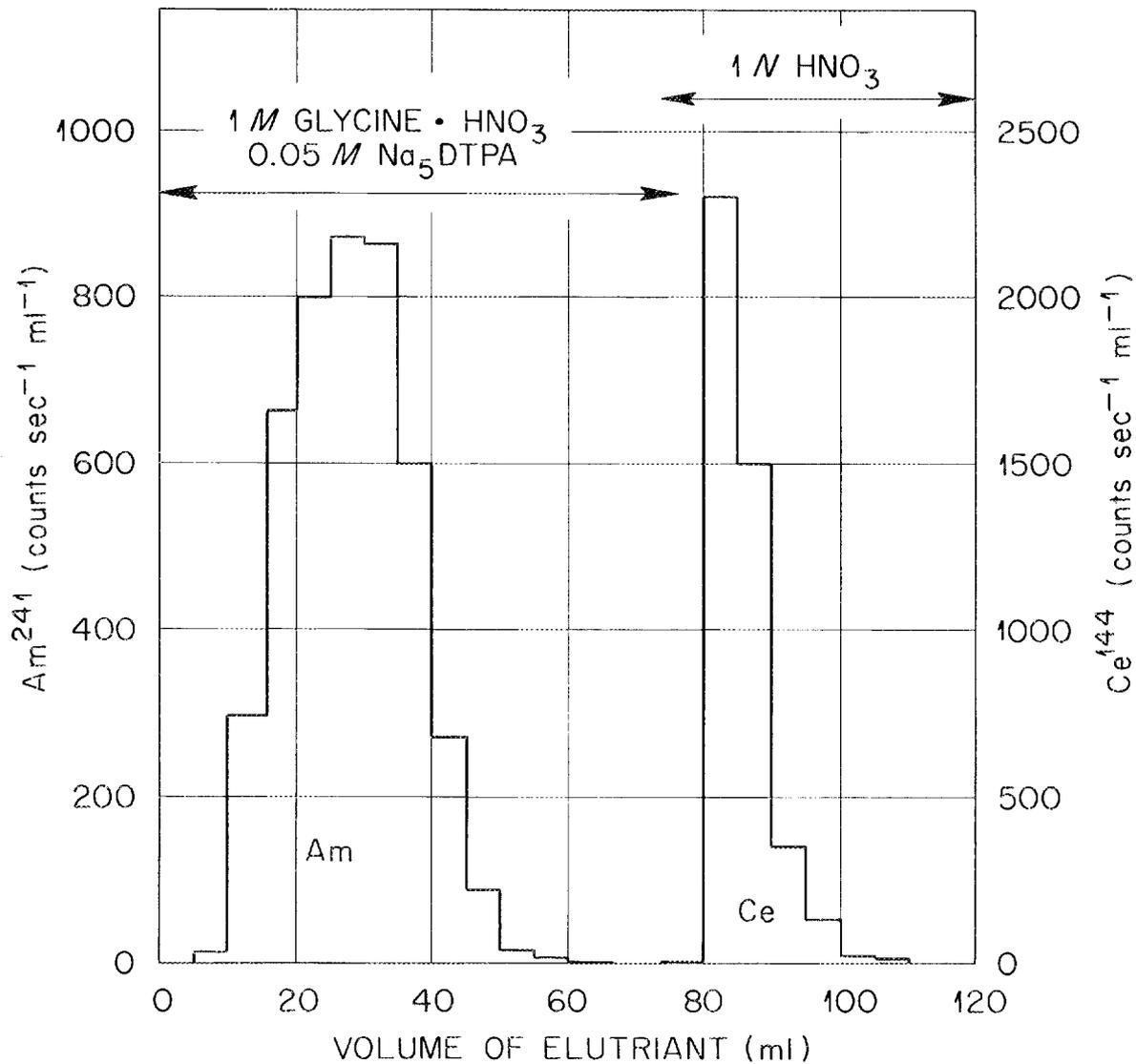
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Fig. 19. Elution by DTPA in Glycine Nitrate from Extraction Chromatographic Column Separates Americium from Europium. Column Material: 5 ml 0.3 M HDEHP in DIPB on 5 g polyethylene. Eluant: 1 M glycine nitrate, 0.05 M Na<sub>5</sub>DTPA.

Table 5. Extraction of Impurities

Organic Phase: 0.3 M HDEHP in DIPB

Element	$E_a^0$			
	Aqueous Solutions			
	1 M Glycolic Acid	1 M Glycolic Acid 0.025 M $\text{Na}_5\text{DTPA}$	1 M Glycine Nitrate	1 M Glycine Nitrate 0.025 M $\text{Na}_5\text{DTPA}$
Ni	<0.001	<0.001	<0.001	<0.001
Co	<0.001	<0.001	<0.001	<0.001
Al	0.03	<0.001	0.01	<0.001
Cu(II)	$\leq$ 0.007	<0.001	$\leq$ 0.007	<0.001
Cd	<0.001	<0.001	$\leq$ 0.011	<0.001
Pb	<0.001	<0.001	<0.001	<0.001
Sn(II)	<0.001	<0.001	<0.001	<0.001
Fe(III)	~100	~0.01	~50	0.2
Ag	0.043	0.23		
Sr	0.05	0.07	0.002	0.004
Cr(III)	<0.001	0.13	<0.001	<0.001
Mn(II)	0.021	0.14	0.028	0.07
Zn	5.0	0.043	$\leq$ 0.007	0.13
Zr-Nb	65	~0.01	ppt.	ppt.
Ru	<0.01	<0.01	<0.01	<0.01

Using a different diluent in the americium-curium extraction cycle would increase the extraction of these elements to an extent not yet studied.

#### 4.5 Effects of Irradiation on Group Separation

The effects of gamma irradiation on aqueous phases and of alpha irradiation on entire extraction systems were tested (1) by exposing aqueous solutions to gamma radiation from a  $^{60}\text{Co}$  source for various lengths of time and using them in extraction experiments, and (2) by performing extraction with solutions containing  $^{140}\text{La}$  and large concentrations of  $^{242}\text{Cm}$ .

##### 4.5.1 Effects of Gamma Irradiation

At 1 M glycolic acid, 0.025 M  $\text{Na}_5\text{DTPA}$  solution was tested for the extraction of americium, cerium, and europium after exposure to various doses of gamma irradiation. Destruction of the  $\text{H}_5\text{DTPA}$  by irradiation slowly increased the susceptibility of americium to extraction by 0.3 M HDEHP in DIPB so that after a dose of 95 whr/liter, the Ce/Am separation factor was reduced from about 100 to 33 (Fig. 20). Exposure of a 1 M glycine nitrate solution to 9 whr of gamma irradiation per liter increased the extraction of americium by 15% and that of cerium by 33%, thus increasing the separation factor between these elements.

##### 4.5.2 Effects of Alpha Irradiation

Extraction experiments were performed (in cooperation with R. D. Baybarz) in which the aqueous solutions contained  $^{140}\text{La}$  and sufficient concentrations of  $^{242}\text{Cm}$  to give a heavy dose of alpha irradiation within a reasonable time. Data on extraction by 0.3 M HDEHP in DIPB from 1 M glycolic acid—0.1 M  $\text{Na}_5\text{DTPA}$  after various periods of contact are given in Fig. 21, and from 1 M glycine nitrate—0.1 M  $\text{Na}_5\text{DTPA}$  in Fig. 22. The glycolic acid system was less sensitive to radiation than the glycine nitrate system. In the first case, the La/Cm separation factor was increased from 50 to 60 by 100 whr/liter and reduced to 33 by 440 whr/liter. For the 1 M glycine nitrate—0.1 M  $\text{Na}_5\text{DTPA}$  system, the La/Cm separation factor increased from 120 to 125 in the first 80 whr/liter exposure and

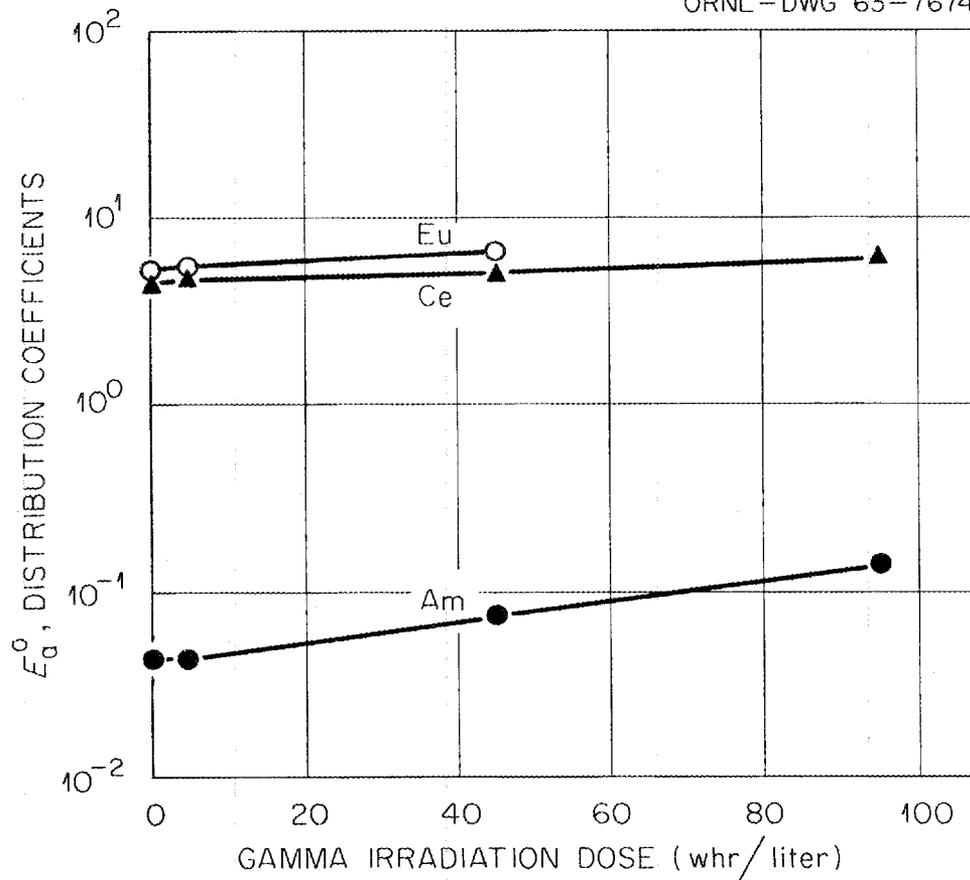
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Fig. 20. Gamma Irradiation Slowly Increases Extractability of Americium from Solution Containing DTPA. Extractant: 0.3 M HDEHP in DIPB. Aqueous phase: 1 M glycolic acid, 0.025 M  $\text{Na}_5\text{DTPA}$ .

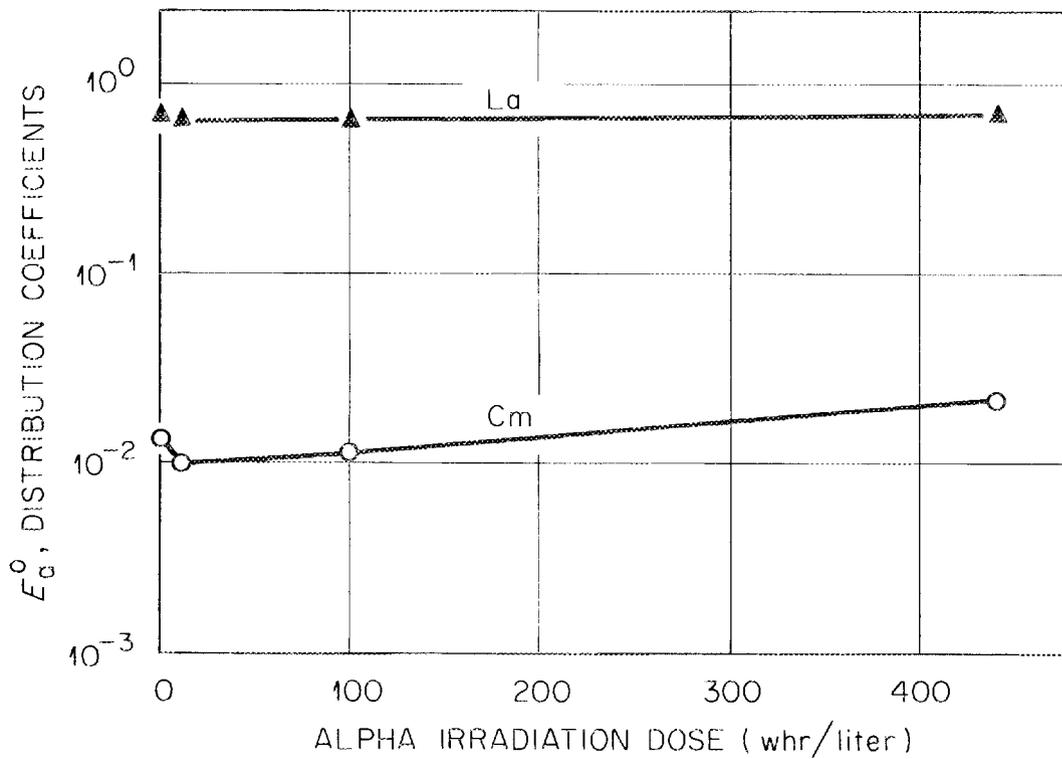
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Fig. 21. Alpha Irradiation Slowly Increases Extraction of Americium from Glycolic Acid Solution Containing DTPA. Extractant: 0.3 M HDEHP in DIPB. Aqueous phase: 1 M glycolic acid, 0.1 M  $\text{Na}_5\text{DTPA}$ .

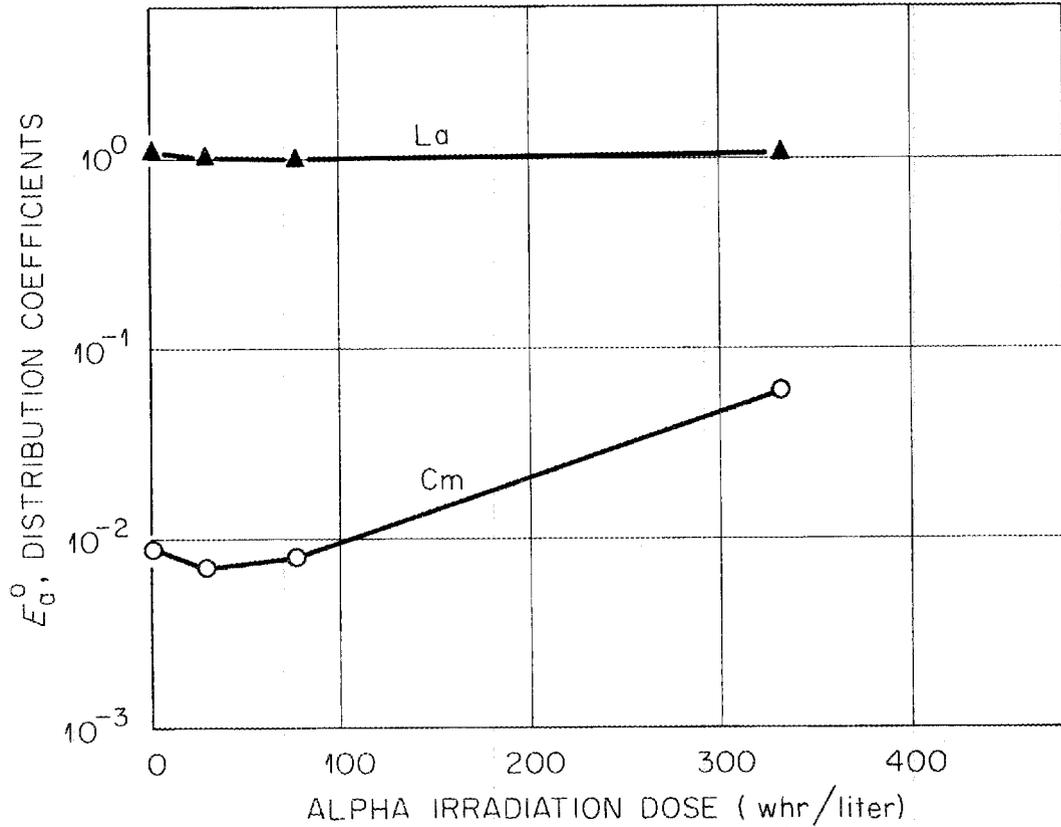
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Fig. 22. Alpha Irradiation Increases Extraction of Americium More Rapidly from Glycine Nitrate Solution than from Glycolic Acid (cf. Fig. 21). Extractant: 0.3 M HDEHP in DIPB. Aqueous phase: 1 M glycine nitrate, 0.1 M  $\text{Na}_5\text{DTPA}$ .

then decreased to 18 when the exposure reached 330 whr/liter. Maximum expected exposures of solutions between addition of  $\text{Na}_5\text{DTPA}$  and completion of the group separation are considerably less than 100 whr/liter.

#### 4.6 Freedom from Corrosion by Process Solutions

One advantage of this method of separation is that it does not require the use of corrosive chemicals. In a simple static test of corrosion, sections of stainless steel pipe were immersed in various possible process solutions and tested for loss of weight after three successive one-tenth-year periods (Table 6). The presence of DTPA in the glycolic acid solution increased the corrosion rate, but the average value of less than 1 mil/yr should be highly satisfactory. In the glycine nitrate solution, the presence of DTPA decreased the somewhat higher corrosion rate, probably because of an increase in pH. Further tests are being made with other probable process solutions of composition likely to be encountered in practice.

Table 6. Rates of Corrosion of Stainless Steel

Aqueous Solution	Corrosion Rate (mils/yr)		
	First Period	Second Period	Third Period
1 <u>M</u> Glycolic acid	<0.01	0.24	0.056
1 <u>M</u> Glycolic acid, 0.025 <u>M</u> $\text{Na}_5\text{DTPA}$	0.05	0.61	0.22
1 <u>M</u> Glycine nitrate, pH 1.9	1.8	1.8	1.9
1 <u>M</u> Glycine nitrate, 0.025 <u>M</u> $\text{Na}_5\text{DTPA}$ , pH 2.1	0.41	0.52	0.47

#### 4.7 Extractions by HDEHP from Aqueous Solutions Containing Aminopolyacetic Acids other than DTPA

##### 4.7.1 Extractions by HDEHP from Solutions Containing Nitrilotriacetic Acid (NTA)

The simplest aminopolyacetic acid studied was nitrilotriacetic or iminotriacetic acid (NTA). In extractions by 0.3 M HDEHP in DIPB from aqueous solutions 1 M in glycolic acid and containing various concentrations of trisodium nitrilotriacetate ( $\text{Na}_3\text{NTA}$ ), a Ce/Am separation factor of 18 was reached when the  $\text{Na}_3\text{NTA}$  concentration was 0.2 M (Fig. 23). Cerium was less extractable than europium.

##### 4.7.2 Extractions by HDEHP from Solutions Containing Hydroxyethylethylenediaminetriacetic Acid (HEDTA)

In extractions by 0.5 M HDEHP in DIPB from 1 M glycolic acid containing various concentrations of trisodium hydroxyethylethylenediaminetriacetate ( $\text{Na}_3\text{HEDTA}$ ) up to 0.2 M, the maximum Ce/Am separation factor was about 25 (Fig. 24). Europium was more extractable than cerium under all conditions.

In extractions by 0.5 M HDEHP in Amsco 125-82 modified by 10% tri-decyl alcohol (TDA) from 1 M glycolic acid containing  $\text{Na}_3\text{HEDTA}$ , the maximum Ce/Am separation factor was about 28, and there was little difference between extractions of cerium and europium (Fig. 25).

In extraction by 0.5 M HDEHP in DIPB modified by 10% TDA from 1 M glycolic acid—0.1 M  $\text{Na}_3\text{HEDTA}$  at various pH values, yttrium was more extractable than all the lanthanides, including lutetium (Fig. 26). In the range of maximum Ce/Am difference, there was much more difference between lutetium and europium than between europium and cerium. These data indicate the possibility of a new method for the separation of yttrium from the lanthanides.

##### 4.7.3 Extractions by HDEHP from Solutions Containing Ethylenediaminetetraacetic Acid (EDTA)

Extraction by 0.5 M HDEHP in DIPB from 1 M glycolic acid 0.01 molar in disodium ethylenediaminetetraacetate ( $\text{Na}_2\text{EDTA}$ ) gave Ce/Am and Eu/Am separation factors of 9 and 65. When the diluent was Amsco 125-82, the

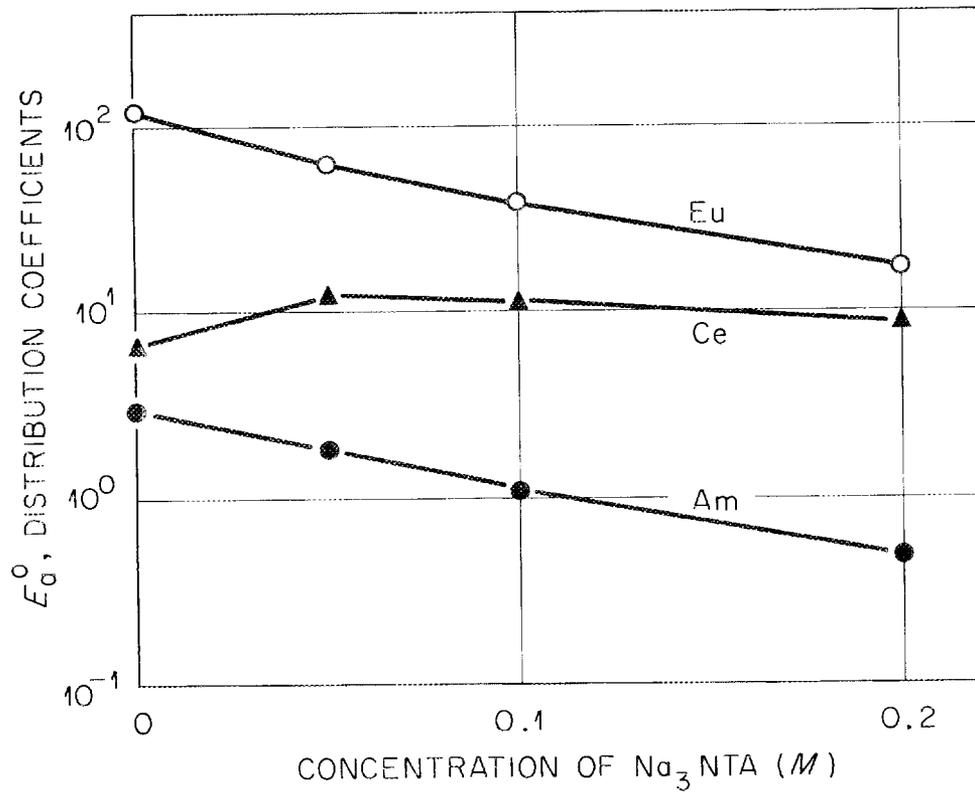
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Fig. 23. NTA Gives Much Smaller Separations than DTPA (cf. Fig. 5).  
Extractant: 0.3  $M$  HDEHP in DIPB. Aqueous phase: 1  $M$  glycolic acid,  
variable  $\text{Na}_3\text{NTA}$  concentration.

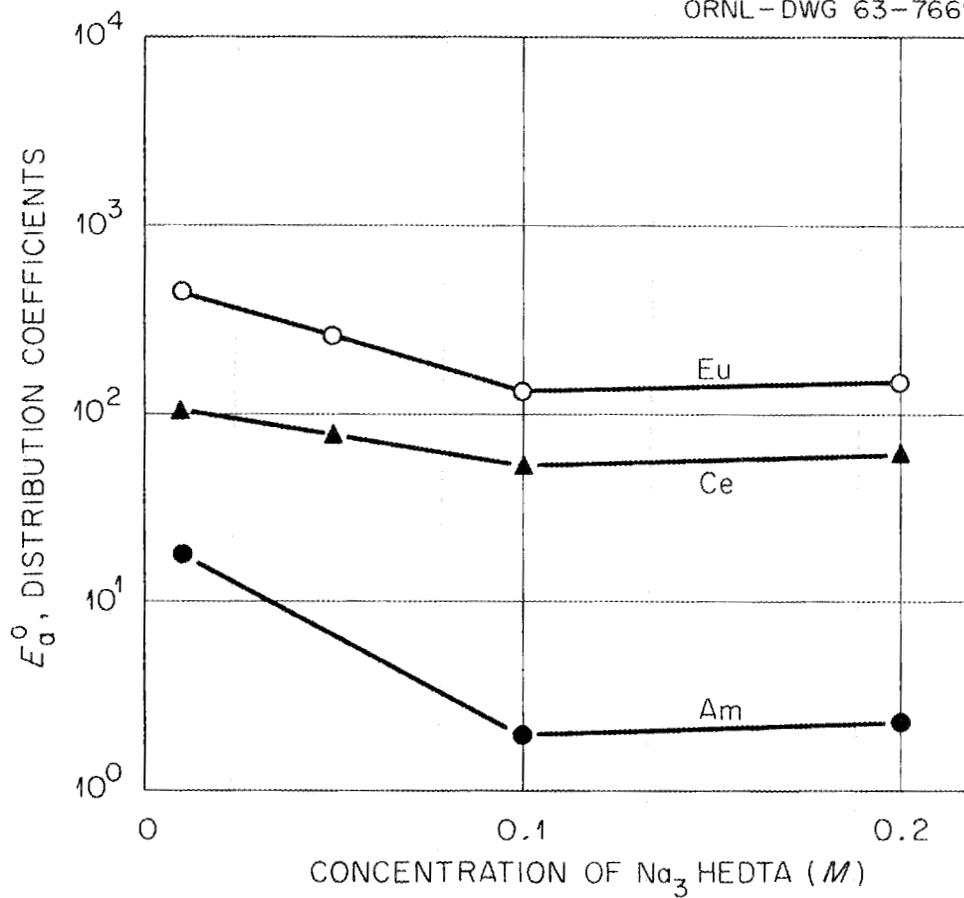
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Fig. 24. HEDTA Gives Separations Intermediate Between Those of NTA and DTPA (cf. Figs. 5 and 23). Extractant: 0.5 M HDEHP in DIPB. Aqueous phase: 1 M glycolic acid, variable  $\text{Na}_3\text{HEDTA}$  concentration.

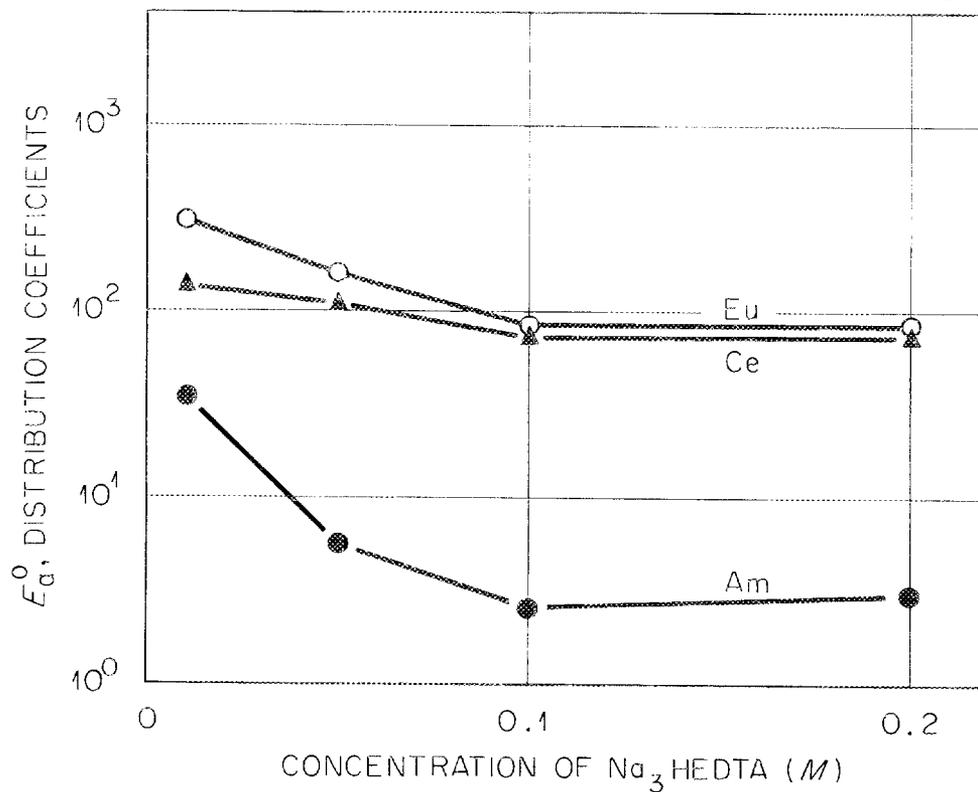
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Fig 25. Extractions by HDEHP in Modified Aliphatic Diluent from HEDTA are Similar to Those with DIPB Diluent (cf. Fig. 24). Extractant: 0.5 M HDEHP in Amsco 125-82 plus 10% TDA. Aqueous phase: 1 M glycolic acid, variable  $\text{Na}_3\text{HEDTA}$  concentration.

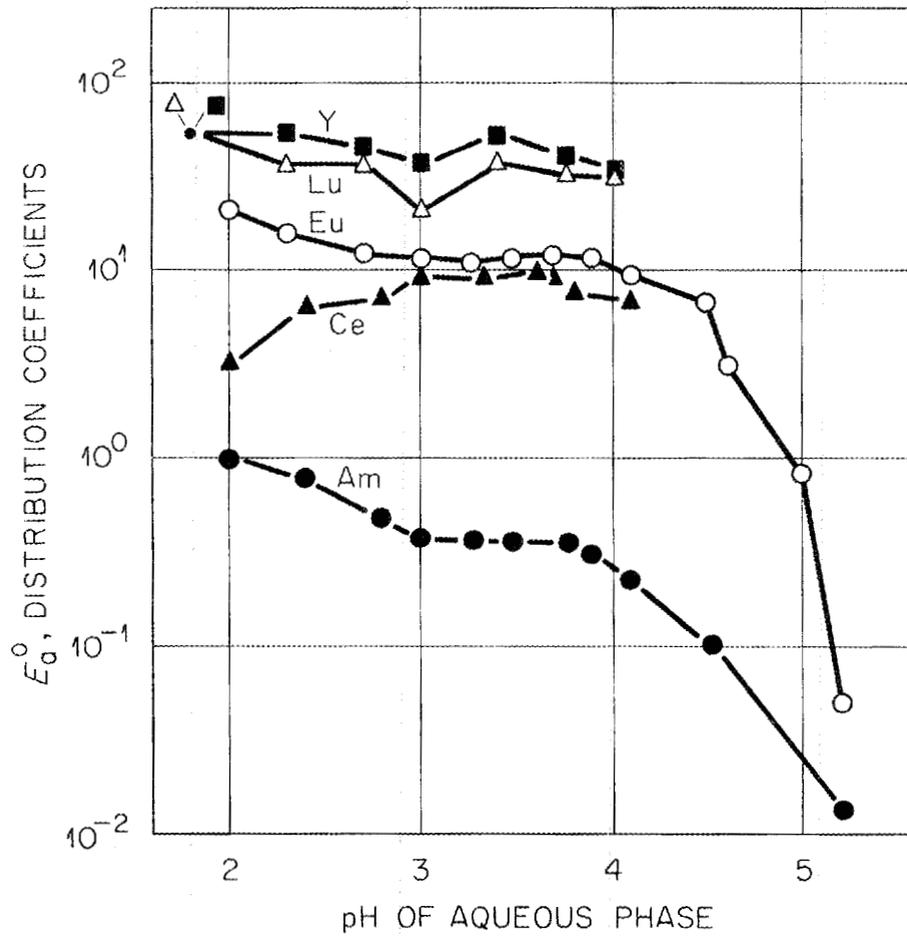
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Fig. 26. In Extractions by HDEHP in a Modified Aliphatic Diluent from HEDTA, Yttrium is More Extractable than all the Lanthanides, Which Extract in Reverse Order of Atomic Numbers. Extractant: 0.5 M HDEHP in Amsco 125-82 plus 10% TDA. Aqueous phase: 1 M glycolic acid, 0.1 M  $\text{Na}_3\text{HEDTA}$ , variable pH.

corresponding separation factors were 9 and 22. The extraction data indicated a strong ability to complex americium preferentially, but solubility was too low for useful application of this reagent. It might be useful in a different carboxylic acid.

#### 4.7.4 Solutions Containing 1,2-Diaminocyclohexanetetraacetic Acid (DCTA)

In a first attempt to prepare a solution 1 M in glycolic acid and 0.1 M in tetrasodium 1,2-diaminocyclohexanetetraacetate, extensive precipitation occurred immediately. In a second attempt, a solution was obtained, but the acid, left unused at 25°C, slowly crystallized over a period of several days. No extractions were made from this solution.

#### 4.7.5 Extractions by HDEHP from Solutions Containing Triethylenetetraminehexaacetic Acid (TTHA)

Extractions were made of americium, cerium, and europium by 0.3 M HDEHP in diethylbenzene (DEB) from 1 M glycolic acid solutions containing small concentrations of hexasodium triethylenetetraminehexaacetate ( $\text{Na}_6\text{TTHA}$ ) up to 0.024 M. The extraction of cerium (Fig. 27) was almost identical with that previously found from solutions containing DTPA in the same concentration range, but the extraction of americium was slightly higher from the solutions containing TTHA, thus giving a somewhat smaller separation factor. Higher concentrations of  $\text{Na}_6\text{TTHA}$  were not studied because of lack of material.

### 4.8 Extractions of Lanthanides and Americium from Simple Carboxylic Acid Solutions

Results from a study of extraction of americium, curium, and some lanthanide elements by dialkylphosphoric acids from solutions of simple carboxylic acids without additional complexing agents have been reported.<sup>6</sup> They may be summarized as showing that carboxylic acids usually caused a shift of the extractabilities of the actinides relative to the lanthanides. The effects on the extractability of americium relative to the extractabilities of cerium and europium are illustrated by a few examples in Fig. 28, where the extractability of americium is assigned a value of 1. The illustration represents relationships found when the organic diluent

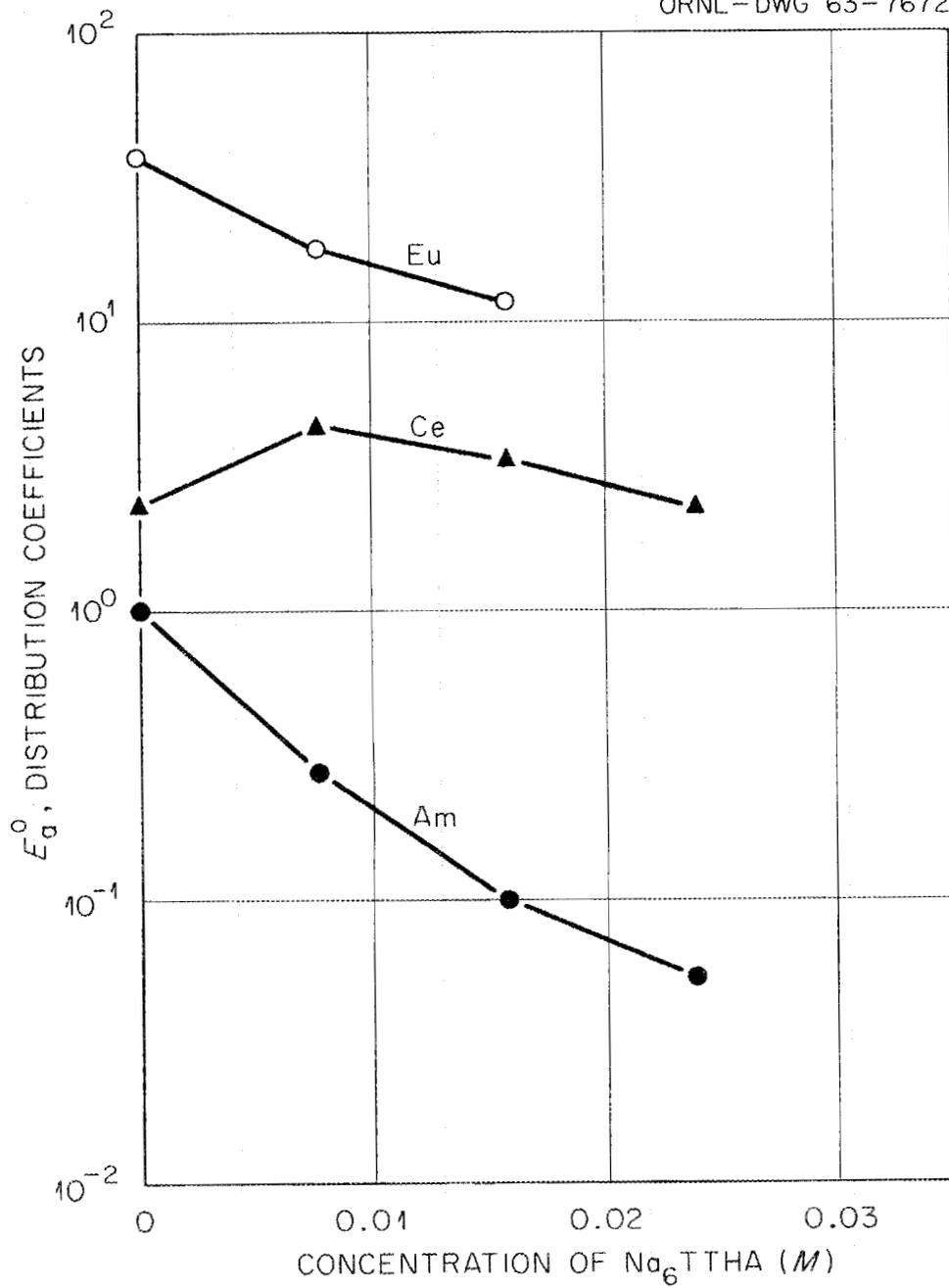
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Fig. 27. TTHA is a Less Effective Group Separator than DTPA at Low Concentrations (cf. Fig. 6). Extractant: 0.3 M HDEHP in DEB. Aqueous phase: 1 M glycolic acid, variable  $\text{Na}_6\text{TTHA}$  concentration.

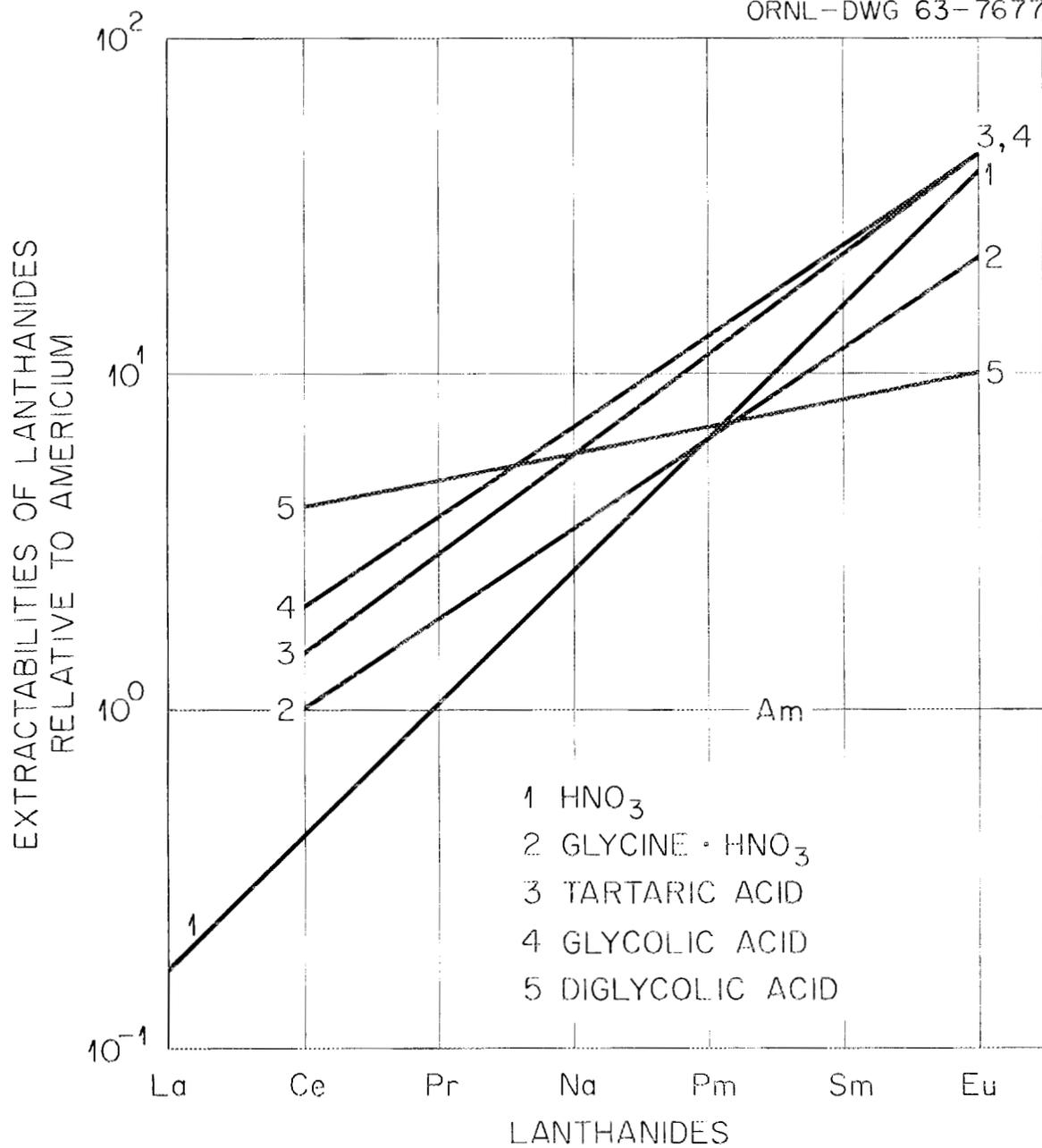
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Fig. 28. Extractabilities of Lanthanides Relative to Americium by Di(2-ethylhexyl)phosphoric Acid are Shifted by Presence of Carboxylic Acids Without Aminopolyacetic Acids.

was diisopropylbenzene; other diluents would have different effects. It was already well known that extraction by solutions of di(2-ethylhexyl)-phosphoric acid from dilute mineral acids gives a nearly constant separation factor of 2.5 between adjacent lanthanides and that americium is homologous with praseodymium in this case.<sup>2</sup> No variation caused by choice of diluent has been reported.

In extractions from a solution 1 M in glycine nitrate, americium was similar to cerium, while the difference between europium and americium was only about half as large as in extraction from dilute nitric acid. These ratios, especially between europium and americium, varied with the diluent.

In extractions from tartaric acid, cerium was about 1.5 times as extractable as americium, while europium was about 40 times as extractable as americium, not much different from the relative behavior of the latter two elements in extraction from mineral acids. Glycolic acid gave a somewhat greater shift for cerium — to a factor of 2 over americium. Several other carboxylic acids, including formic, lactic, malic, malonic, and  $\alpha$ -hydroxyisobutyric acids gave results within the range illustrated.

The greatest departure from the behavior of mineral acids was found in the case of diglycolic (oxydiacetic) acid. Here, there was a factor of 4 between the distribution coefficients of cerium and americium under a great variety of conditions, though the factor between europium and americium varied with the composition of the extractant. Preliminary results showed that extraction from equimolar mixtures of glycolic acid and glycine gave separations between cerium and americium equal to those from diglycolic acid.

More recent tests showed that these differences between the lanthanides and americium can be increased still further in some cases by adjustment of the pH of the aqueous solutions. For example, increasing the pH of a 1 M glycolic acid solution to 3.5 increased the Ce/Am separation factor to about 6, but it caused a somewhat smaller increase in the case of lactic acid (Fig. 29). Increase of pH caused a greater increase in the extraction of all these elements from lactic than from glycolic acid.

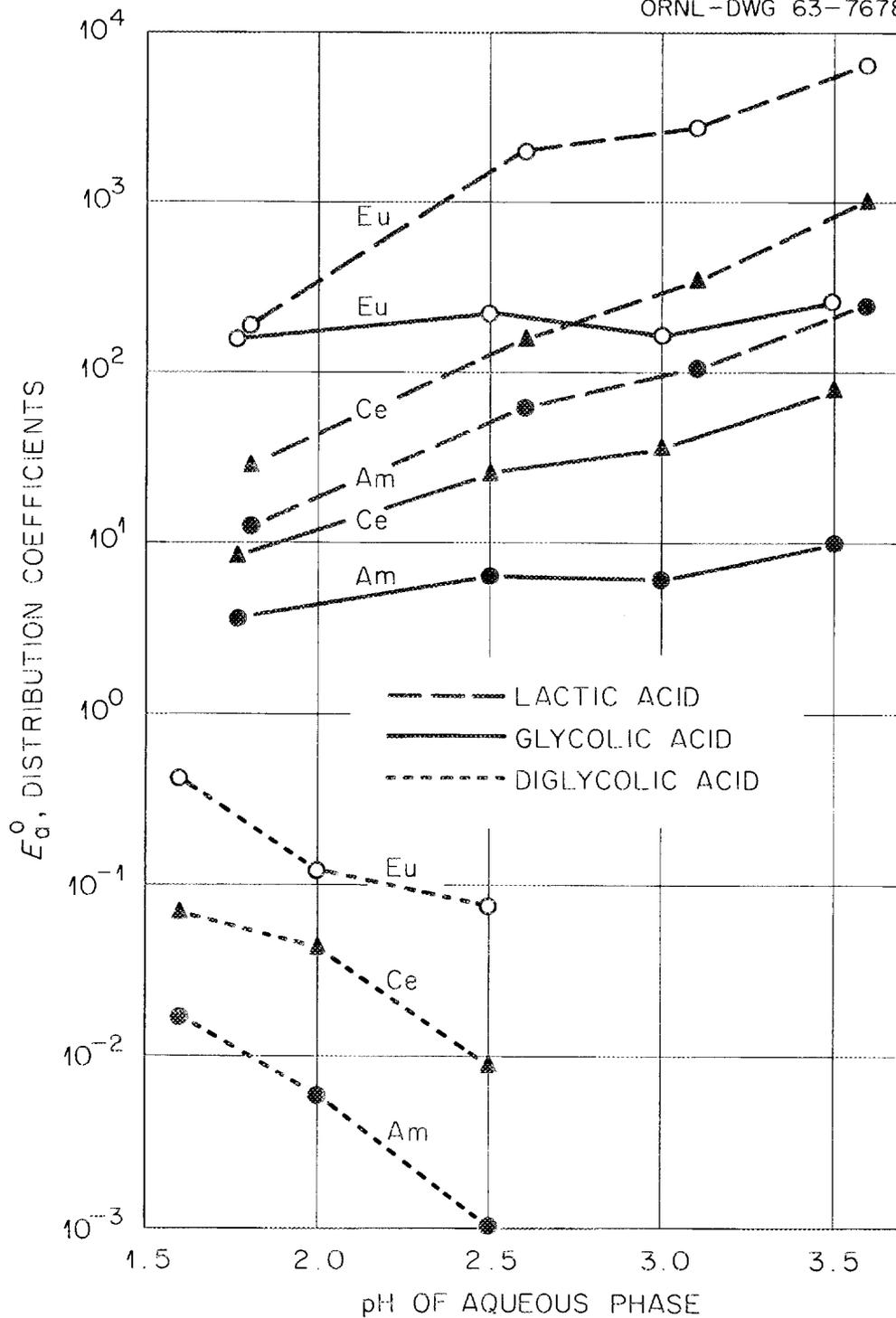
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Fig. 29. Effects of pH Adjustment on Extraction of Americium and Lanthanides from Carboxylic Acids Varies with Acid Identity. Extractant: 0.3 M HDEHP in DIPB. Aqueous phases: 1 M carboxylic acids, variable pH.

In extractions from diglycolic acid, increase of pH greatly decreased all extractions, while the Ce/Am separation factor increased to nearly 9 at pH 2.5. All extractions were too low for practical application, though they could be increased to possibly practical level by increasing the concentration of HDEHP and changing the diluent.

Some of these extractions might have been developed into useful processes for the separation of americium and curium from at least the heavier lanthanides. Such a process could be combined with another process for the separation of americium and curium from the lightest lanthanides, such as extraction by tributyl phosphate from nitric acid, in which americium is like promethium.<sup>7</sup> However, the addition of aminopolyacetic acids gives so much larger separation factors that little consideration has been given to a process involving only the simple carboxylic acids.

#### 4.9 Extraction by Monoacidic Phosphonates from Solutions Containing DTPA

Monoacidic phosphonates also extract the trivalent lanthanides more effectively than they extract americium and curium. They were studied as possible alternatives to monoacidic organophosphates in the separation of the two groups of elements and as more powerful extractants for the recovery of americium and curium from the aqueous raffinates of the separation cycle.

##### 4.9.1 Group Separation by Extraction with 2-Ethylhexyl Phenylphosphonic Acid (HEH[ $\phi$ P])

Separation of the trivalent actinide and lanthanide groups by extraction with dilute hydrocarbon solutions of 2-ethylhexyl phenylphosphonic acid (HEH[ $\phi$ P]) is very similar to that by HDEHP, except that the phosphonic acid gives considerably higher distribution coefficients. In extractions by 0.1 M HEH[ $\phi$ P] in DIPB from a mixed lactic acid—Na<sub>5</sub>DTPA solution, cerium and europium were both about 100 times as extractable as americium when the Na<sub>5</sub>DTPA concentration was 0.04 to 0.20 M (Fig. 30).

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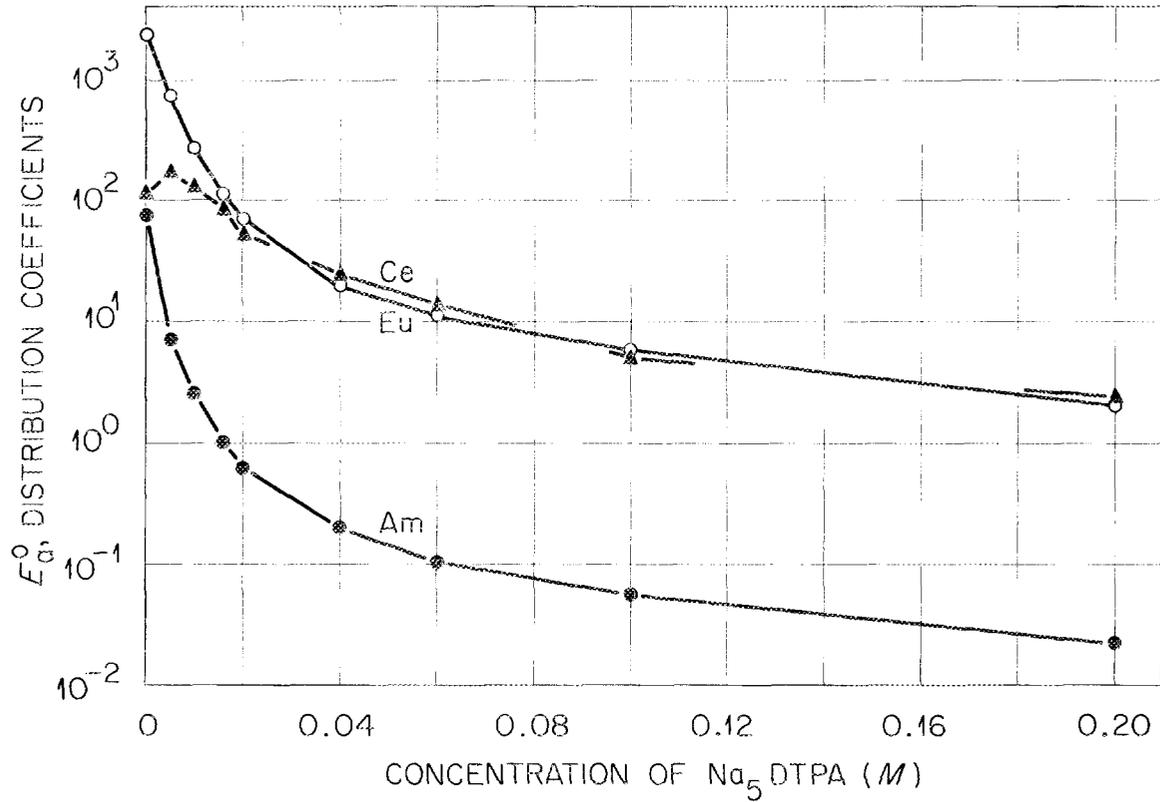


Fig. 30. Group Separations in Extractions from DTPA Solutions with HEH[ $\phi$ P] Are Similar to Those with HDEHP (cf. Fig. 2). Extractant: 0.1 M HEH[ $\phi$ P] in DIPB. Aqueous phase: 1 M lactic acid, variable Na<sub>5</sub>DTPA concentration.

#### 4.9.2 Extraction by Decyl Decylphosphonic Acid

The extraction of americium, cerium, and europium by decyl decylphosphonic acid (HD[DP]) was tested only briefly. Extraction by 0.3 M HD(DP) in DIPB separated the two groups effectively when the aqueous solution was 1 M in glycolic acid but not when it was 1 M in glycine nitrate (Table 7). Distribution coefficients were much lower than those in extraction by HEH[OP] under the same conditions.

Table 7. Extractions by Decyl Decylphosphonic Acid from Glycolic Acid and Glycine Nitrate Containing Diethylenetriaminepentaacetic Acid

Organic phase: 0.3 M in DIPB

Aqueous Phase	$E_a^0$			Separation Factors	
	Am	Ce	Eu	Ce/Am	Eu/Am
1 M Glycolic acid, 0.025 M Na <sub>5</sub> DTPA	0.015	1.48	0.93	100	63
1 M Glycolic acid, 0.05 M Na <sub>5</sub> DTPA	0.011	0.85	0.58	77	53
1 M Glycine·HNO <sub>3</sub> , 0.1 M Na <sub>5</sub> DTPA	0.41	4.6	18	11	45

## 5. CONCLUSIONS

The results of experimental studies show that the lanthanides and yttrium are much more extractable than americium and curium with hydrocarbon solutions of di(2-ethylhexyl)phosphoric acid or 2-ethylhexyl phenylphosphonic acid from aqueous solutions containing diethylenetriaminepentaacetic acid (Talspeak process). Separation factors between the americium-curium pair and the lanthanide group are comparable with those in the Tramex process,<sup>2</sup> though in the opposite direction. There are no obvious reasons why the Talspeak method cannot be applied to a multistage countercurrent process for complete separation of these groups. It should be especially useful for the purification of large quantities of curium isotopes. The degree of separation of the lanthanides from the heavier actinides, including californium, and the optimum flowsheet conditions for purification of these elements along with americium and curium will be determined by other studies now in progress.

Most of the elements likely to occur as impurities are separable in one or more of the three cycles in the Talspeak process. While lactic acid appeared to be the preferable aqueous medium, other carboxylic acids might be used if they are found to have advantages in separation of some elements.

Problems in recovery of the actinides caused by low rates of extraction have been solved by decreasing the pH of the aqueous solution somewhat below that at which the group separation is made. Decreasing the pH also greatly increases the distribution coefficients.

Gamma and alpha irradiation slowly increase distribution coefficients by decomposing the complexing agent. Fortunately, since there is a wide range of complexant concentrations over which group separation factors are nearly constant, high radiation doses can be tolerated without significantly decreasing the high degree of separation obtainable by the method.

The Talspeak process has a potential disadvantage with some feeds since the more extractable lanthanides are present at much higher concentrations than the trivalent actinides and it is necessary to remove the major from the minor constituent. However, preliminary tests with lanthanide concentrations up to several grams per liter have given successful results and have indicated that much higher concentrations could be tolerated.

The separation of lanthanides from the trivalent actinides by extraction chromatography should be very useful for processing at least small quantities of the actinides, especially in analytical applications.

Preliminary corrosion tests indicate that stainless steel is a suitable material for use in process equipment; so, it is unnecessary to use the more expensive materials that are required for processing the chloride solutions that characterize the Tramex process.<sup>2</sup>

## 6. ACKNOWLEDGMENTS

We are grateful to R. D. Spitz of Dow Chemical Company for samples of aminopolyacetic acids, and especially for sharing his small supply of triethylenetetraminehexaacetic acid. We acknowledge the cooperation

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